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JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

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THE USE OF AN IMPULSE SOURCE FOR SPECTRA EXCITATION DURING THE SPECTROGRAPHIC ANALYSIS OF SILICATES

V. V. Korolev and E. E. Vainshtein

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Two basic approaches are known for the use of spectrographic methods in the analysis of silicate rocks. The first approach [1, 2] is to get the sample into solution and then analyze it by the usual methods; the second [3-5] is applicable to the analysis of solid rock powders, but requires that the test material be diluted several times with a buffer mixture. Sometimes, with the aim of increasing the accuracy of a determination, it is recommended that additional apparatus be used which stabilizes the operation of the spectra excitation sources, such as magnetic blowing [6], blowing the air along electrodes arranged vertically [7-9] etc. While these methods are characterized by operations which are tedious and difficult, the accuracy attained by their use is relatively low, and, according to the results given by various authors, are of the order of 4 – 7% and 6 – 10%. This factor limits, and sometimes, complicates the wide practical application of these methods.

High-temperature impulse sources of spectra excitation, as experiments carried out in our laboratory have shown, enable the accuracy of the spectrographic analysis of silicates to be increased.

Of a number of impulse sources which have been suggested in the last ten years [10-17], our attention was attracted to one suggested as long ago as 1945 by Levintov [10-13] for carrying out spectrographic determination of metalloids. Impulse intensification of the current of a stationary arc was realized by means of a periodic discharge from a high-voltage condenser through it. We used a high-temperature spectra excitation source of this type in the work described in the present article.

The excitation source is shown schematically in Fig. 1. The stationary element of the setup is a d.c. arc with carbon electrodes fed from a mercury rectifier (U_p = 270 volts); the impulse is supplied by a condensed spark from a IG-2 generator. The optimum operating conditions of the source were chosen experimentally in accordance with the results of work carried out by Sobolev [18 – 19] and Raiskii [20]. A minimum value of the inductance was chosen (L = 0), while the capacity was 0.02 μF, and the value of the discharge gap was varied within the limits 0.5 to 3 mm. In order to protect the d.c. circuit from current impulses, use was made of a filter constructed from two symmetrically arranged self-inductances, with a total inductance of 120 μH and a capacity of 1 μF (U_{times} = 400 volts). As is evident from the schematic diagram, at the same time as the knife-switch 4 is switched on, during light contact of the electrodes with one another, a magnetic starter 5 comes into operation, the magnetic starter being connected into the d.c. circuit in parallel with an additional resistance 6. This leads to short-circuiting of terminals 7, through which a potential is applied to the inlet of the primary winding of the high-voltage transformer of the generator.

As a result of the superposition of a spark discharge on the arc, impulse intensification of the current occurs, the strength of which, according to preliminary measurements, amounts to 400 – 500 amps.

An impulse arc is characterized by a number of properties, which profitably distinguishes it from the usual type of d.c. arc. Thanks to this, the accuracy of spectrographic determinations is increased.

A simplified technique based on the application of the well-known Ornstein method [21-22] was used for establishing the temperature of the impulse arc. The method is applicable to sources in which, during a state

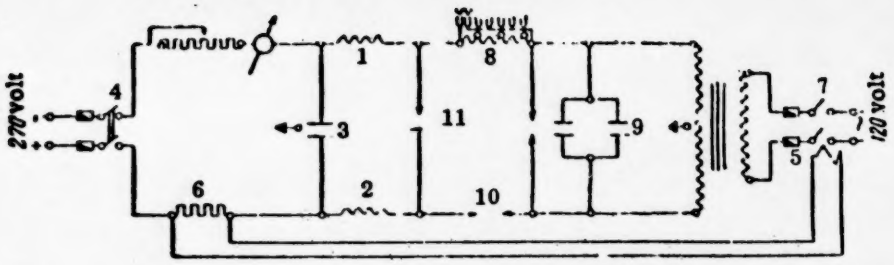

Fig. 1. Scheme of an impulse source of spectra excitation:
1-2) Inductance of the protective filter; 3) capacity of the protective filter; 4) knife-switch; 5) magnetic starter; 6) resistance; 7) terminals; 8) inductance of the spark generator, 9) capacity of the spark generator; 10) auxiliary discharge gap; 11) operating discharge gap.

of equilibrium, a Boltzmann distribution of the atoms and ions in the plasma holds good. In cases where the absolute values of the probabilities of transitions for various spectral lines are not known, this method can still be used to give an approximate idea of the temperature of the source by comparing it with other sources whose temperature is known. Determination of the temperature of the test source is carried out by means of the relation:

$$2{,}3\lg\frac{I_x}{I_s}=2{,}3\lg\frac{N_{0x}}{N_{0s}}+\frac{E}{K}\left(\frac{1}{T_s}-\frac{1}{T_x}\right),$$

where I_x and I_s are the intensities of the lines of an element, the energies of the upper levels (E) of which are known; T_x and T_s are the corresponding temperatures of the test and standard source; K is the Boltzman constant. This relationship is presented graphically within the coordinates $\log\frac{I_x}{I_s}-E$. The slope found in this way enables one to find the temperature T_x required, directly from the known value of T_s.

In order to measure the temperature of the impulse arc, its central part was reflected onto the slit of a spectrograph by means of a two-lens illumination system. The electrodes were covered with ZnO containing 0.3% Bi_2O_3. Measurements were carried out on the basis of the Bi I lines, the energies of whose upper levels are known from the work of Sobolev [19].* The temperature of the standard arc, operating in ZnO vapor was taken to be equal to 6100°K on the basis of Brinkman's work [23]. Both the d.c. arc and the impulse arc were operated at 10 amps. and 270 volts. The relationship established experimentally between logarithm $\frac{I_{Bi}\text{ (impulse arc)}}{I_{Bi}\text{(arc)}}$ and E is shown in Fig. 2. From the slope of the straight line which was 0.58, it was found that the temperature of the impulse arc approximated 9800° K.

The extent of the changes in the line intensities along the interelectrode gap in the impulse arc and in the usual arc, for the lines Zn I 3075.9 and Zn II 2557.9 A, is shown in Fig. 3. In contrast to the usual arc, for which, in our experiments, there was observed a regular change in the intensity of the spectral lines of the ionized atoms on going from anode to cathode, and a characteristic intensification of the intensities in the region near the electrode, in the impulse arc, the intensity of these lines, just like the intensity of the lines developed during excitation of the atoms of the elements, remains almost constant along all the interelectrode gap. Spectrograms obtained under identical conditions, using an impulse arc and an ordinary d.c. arc, show that in the first instance,

* The temperature of a d.c. arc operating in NaCl vapor as measured by this method, proved to be 4600°K. This is in good agreement with the latest results of Kolesnikov and Pokhil'ko [24].

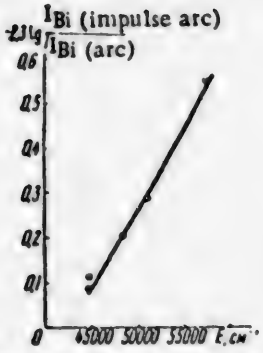

Fig. 2. Determination of the temperature of the impulse arc

there occurs a significant increase in the total brightness of the spectra. Under such conditions, there is observed an increase in the number of lines of the ionized atoms and an increase in their intensity (see Table 1).

The high temperature of the source, the uniformity of the spatial distribution of the excited atoms and ions in its interelectrode gap, and some of the characteristics of the way in which the material passes into the active zone of the source* have a favorable effect on the reproducibility and accuracy of spectrographic determinations. During work with an impulse arc, the relative intensity of lines of different elements is considerably less than in a normal source, and depends on the extent of their homogeneity. One can readily be convinced of this, for example, by examining the curve shown in Fig. 4. Here is shown the relation between the difference in blackening of the lines Na 5889.9 (2.1 ev) and Cu 5700.2 A (3.82 ev) and changes, over a fairly wide range, in current strength and in the distance between electrodes in the impulse arc. A constant value for ΔS is not observed in an ordinary d.c. arc.

A Technique for the Analysis of Silicates. A d.c. impulse arc permits one to extend the number of basic components of silicate rocks that can be determined simultaneously, to simplify analysis, and, what is most important, to increase its accuracy and reproducibility. The method described below has been designed with the object of carrying out a simultaneous quantitative determination, on one aliquot of test material, of nine basic components of rocks of different mineralogical and chemical composition, for contents of these components ranging from 0.5 to 80%. These elements include: Si, Ti, Al, Fe, Ca, Mg, Mn, Na, and K. Prior to analysis, with the object of removing absorbed water, the sample is dried for one hour at 105 – 110 deg. In order to reduce fractional evaporation of the elements to a minimum, the test material is diluted in the proportion of 1:1:2 with cupric oxide and carbon powder. The mixture obtained is carefully mixed for 10 – 15 minutes in an agate mortar, and then 30 mg of it placed in the anode cavity (3.5 × 4 mm). The cathode is a cylindrical carbon rod 2 mm in diameter. In order to prevent sputtering from the electrode cavity, the sample is moistened beforehand with two drops of distilled water and then dried. The spectra are excited by means of an impulse arc operating at 10 amps. and 270 volts. The IG-2 spark generator is controlled to operate according to a composite system at L = O; c = 0.02 μF and an auxiliary spark gap of 0.5 mm. Under these conditions, 4 – 5 discharges of the condenser occur during the half-period of the current. The central part is projected by means of a three lens illumination system, through an intermediate diaphragm 2, onto the slit of the ISP-22 and ISP-51 spectrographs (the camera has a focal length of 270 mm). For convenience in carrying out photometric measurements, a two-stage attenuator is fitted in front of the spectrograph slits; exposure 1.5 minutes. During this time (see curves in Fig. 5) there occurs almost complete evaporation of the elements to be determined from the test sample. The spectra are registered on "Reproduction" plates with a sensitivity of 1.4 GOST units, and "Infrachrome 760" and plates developed in a D-19 developer.

The analytical lines of the elements, and the corresponding reference lines are given in Table 2. The Table also contains information on the concentration ranges of the elements to be determined, within which these lines can be used most expediently.

In order to construct calibration curves and to carry out control determinations, samples of silicate materials were chosen, the composition of which (Table 3) was established by classical chemical methods.**

* The problem of the mechanism of the passage of test material from the electrode crater into the active zone of the impulse source, and the relation between arc and spark conditions of operation is of great practical and scientific interest; it has not been studied enough and is at present being investigated in our laboratory.

** The authors wish to thank N. V. Buianov for his gift of several samples of "Martin" slags which had been analyzed.

TABLE 1

Source \ Spectral line in A	Line blackening							
	Ionized atom				Non-ionized atom			
	Cu I 2837,5 (10,7 eV)	Zn I 2558,0 (10,95 eV)	Zn I 2502,0 (10,95 eV)	C I 2836,7 (16,3 eV)	Cu I 3247,5 (3,82 eV)	Zn I 3075,9 (4,09 eV)	Cu I 2441,6 (5,1 eV)	Zn I 3345,0 (7,78 eV)
Impulse arc	0,20	0,99	0,87	0,33	0,52	0,95	0,96	0,71
d. c. arc	0,02	0,39	0,21	0,05	0,54	0,92	1,01	0,73

Calibration curves for the quantitative determination of silicon, titanium, aluminum, iron, calcium, magnesium, and manganese were constructed on the basis of the blackening of the analytical lines with the coordinates ΔS – logarithm C. During determination of sodium and potassium, as noted already [25], it was found more expedient to use the method of the width of the spectral line.

TABLE 2

Lines of the test element, in A		Lines of the reference element in A		Optimum concentration range, in %
Si	2987,7	Cu	3030,8	10,0—80,0
Ti	3075,2	Cu	3010,8	0,10—2,50
	3186,5		3194,1	
Al	3944,0	Cu	3194,1	0,50—40,0
Fe	2950,2	Cu	3010,8	0,50—3,0
	3024,0		3010,8	3,0—40,0
Ca	3158,9	Cu	3194,1	0,50—9,0
	3180,5		3194,1	8,0—50,0
Mg	2776,7	Cu	3010,8	1,0—40,0
	2802,7		3010,8	0,01—2,0
Mn	2800,1	Cu	3010,8	0,01—1,0
	2933,1		3010,8	0,30—20,0
K	7664,9	Cu	7933,1	0,50—14*
	7798,9		5218,2	
Na	5889,9	Cu	8092,6	0,50—12*
	5895,9		5218,2	

* Where necessary the upper concentration limit can be increased to 30%, while the lower limit can be dropped to 0.1%.

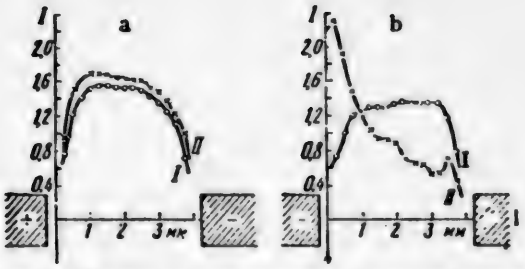

Fig. 3. Change in line intensity of excited atoms (1), and ions (2) along the interelectrode gap of the source for an impulse arc (a) and for a d. c. arc (b).

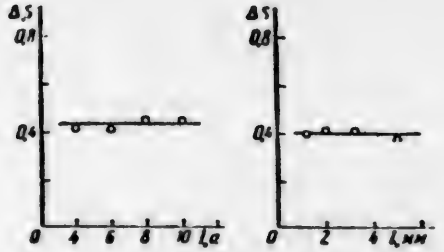

Fig. 4. Relation between the blackening differences of two lines, and changes in current strength, and the distance between electrodes in an impulse arc.

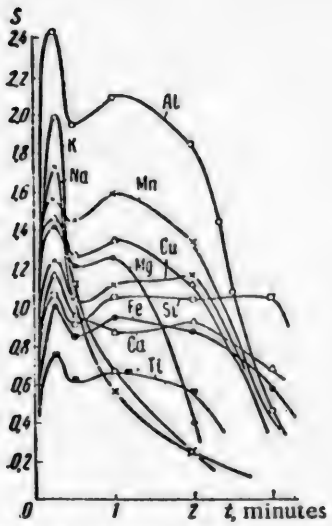

Fig. 5. Curves illustrating passage of elements into the active zone of the impulse arc.

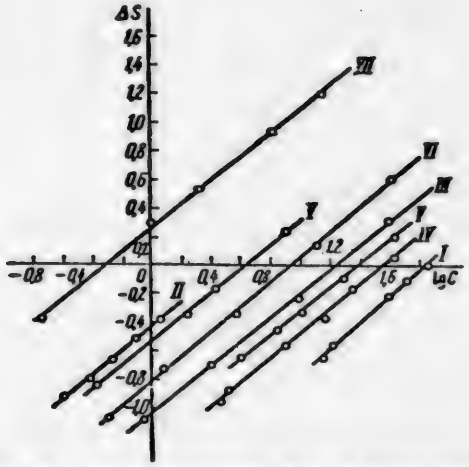

Fig. 6. Calibration curves for the determination of the oxides of: Si (I); Ti (II); Al (III); Fe (IV); Ca (Va, b); Mg (VI); Mn (VII) in rocks.

The appropriate curves are shown in Figs. 6 and 7.

Despite the considerable difference in the mineralogical and chemical composition of the samples tested, no mutual effect of the elements on one another could be detected, neither did the bulk composition have any effect on the results of the spectrographic determination. This can be explained, presumably, by the high temperature and the stability of the excitation conditions of the atoms in the source employed, and also by the uniformity of the distribution of the test elements in the interelectrode gap of the impulse arc.

The reproducibility of the method described was evaluated by comparing the results of determination of the contents of the test elements in a number of parallel experiments. In Fig. 8, for example, are given results for five parallel determinations of the contents of the main components, and the blackening differences of the lines relating to these experiments. Results obtained when an ordinary arc was used are given on the right, while the results on the left are those obtained by means of an impulse arc. The reproducibility of the results obtained by means of an impulse arc is almost twice as high as that obtained when using an ordinary arc. The mean arithmetic error (calculated on 5 replicates) varied within the limits 2 to 3%.

TABLE 3

Sample	Mineralogical composition	Chemical composition, in %								
		SiO_2	TiO_2	Al_2O_2	Fe_2O_2	CaO	MgO	MnO	Na_2O	K_2O
Clay	Kaolinite, monothermite quartz, rutile	48.90	2.00	33.02	2.28	0.36	0.25	0.03	—	0.07
Clay marl		32.78	0.38	8.76	3.68	15.30	10.99	—	1.88	1.76
Arkose sandstone	Quartz, feldspar, magnetite	72.44	0.53	9.56	6.97	1.66	1.24	—	—	2.49
Leucocratic granite	Quartz, orthoclase, plagioclase, biotite, magnetite	72.42	0.34	13.65	2.57	1.49	0.52	—	3.33	4.66
Granodiorite	Quartz, orthoclase, plagioclase, hornblende, biotite, magnetite	68.31	0.56	15.18	3.58	3.34	1.38	—	2.99	4.06
Diorite	Plagioclase, pyroxene, amphibole, orthoclase	56.06	0.65	17.31	7.76	6.92	3.60	0.15	2.65	2.59
Nephelinic syenite	Orthoclase, nepheline, alkali amphibole, biotite	57.23	0.46	20.51	2.56	1.68	0.66	—	2.32	12.44
Urtite	Orthoclase, pyroxene	51.08	0.21	25.46	3.64	1.43	0.99	0.11	11.10	3.94
Metamorphic shale	Quartz, bitotite, magnetite, granite	45.52	0.43	9.26	35.73	—	3.74	—	0.05	1.15
Granite	Quartz, orthoclase, plagioclase, biotite	70.90	0.20	12.98	1.90	2.94	0.45	0.09	6.37	0.58
Sham	Pyroxene, granite, quartz	48.14	0.10	0.87	23.6	22.88	0.92	2.41	—	—
Biotitic hornstone	Quartz, biotite, plagioclase, orthoclase	52.2	0.70	18.01	7.17	2.43	1.60	—	4.31	6.25
Quartz monzonite	Plagioclase, amphibole, orthoclase, quartz	63.57	0.42	15.75	4.19	4.77	1.92	0.10	5.02	1.99
Saxonite	Olivine, pyroxene	42.13	0.07	2.43	7.65	2.05	41.34	0.08	—	—
Dunite	Olivine, pyroxene	36.60	0.06	1.87	8.07	1.34	40.40	0.10	—	—
Martin slag		12.15	—	7.85	17.60	42.60	13.75	3.40	—	—
Martin slag		16.72	—	2.43	37.00	30.48	7.91	18.31	—	—
Coal ash		28.16	—	22.73	43.39	2.40	0.76	—	—	—

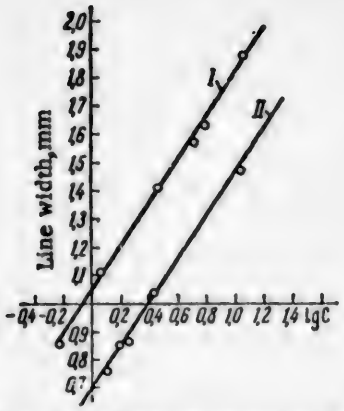

Fig. 7. Calibration curves for the determination of the oxides of: K (I) and Na (II) in rocks, by means of the spectral line width method.

The reliability of the method was checked by comparing the results of chemical and spectrographic determinations of the elements in 60 samples of rock. Some of the results obtained are shown graphically as examples in Fig. 9. The content of the element as determined chemically in the sample is plotted along the abscissa, while the relative values of the deviation of the results of spectrographic determination of the same elements using an ordinary arc 3 and an impulse arc, are plotted along the ordinate. As these results show, the use of an impulse arc permits one to achieve a significant increase in the accuracy of a determination. The maximum deviation between the results obtained by the spectrographic and chemical methods, did not exceed 4% for all the test elements. This error could be reduced by carrying out two-fold photometric measurements on the spectrograms.

As practice in the use of the techniques developed earlier [26, 27] has shown, an impulse source of spectra excitation can also prove useful for the quantitative spectrographic analysis of the main components not only of rocks, but also of other nonmetallic objects. In all these cases, the technique developed distinguished itself from the chemical methods for silicate analysis by the speed with which it can be carried out; it also requires incomparably smaller amounts of test material.

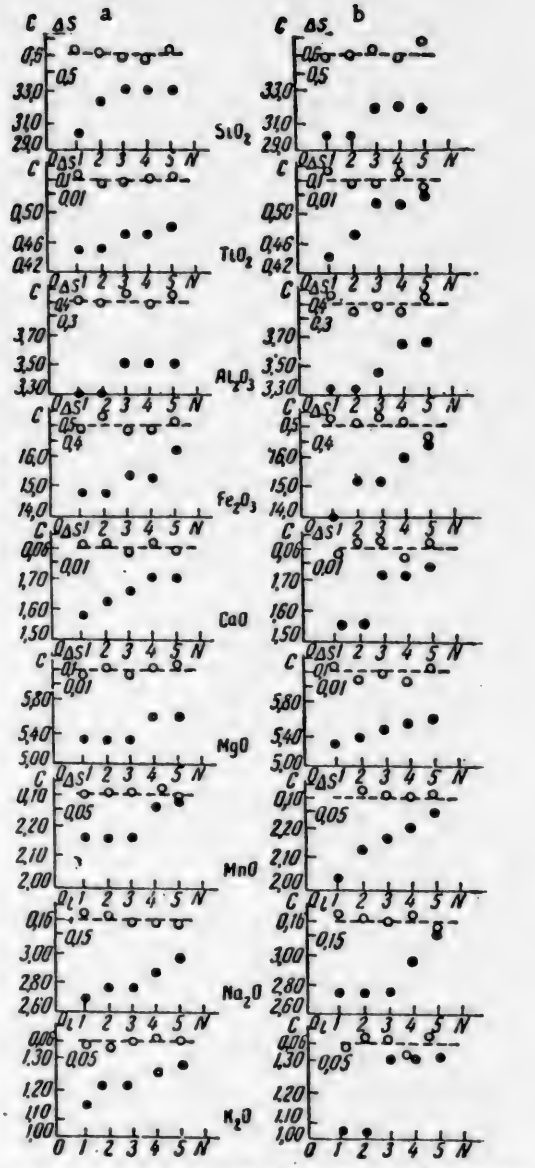

Fig. 8. Reproducibility of the results of spectrographic determination of elements in rocks using an impulse arc (a), and a d. c. arc (b): ●) content of element (C), in %; ○) blackening difference of the lines of the element and of the reference element (ΔS); N) number of experiments; e) line width.

SUMMARY

1. An attempt has been made to use an impulse source for carrying out spectrographic analysis of silicate rocks for their main components. The source described has an operating temperature of about 10,000°K, and is characterized by a considerably more uniform distribution of the excited atoms and ions in the plasma, than in the case of a d.c. arc. The relative intensity of the lines of various elements hardly depends at all on their degree of homology.

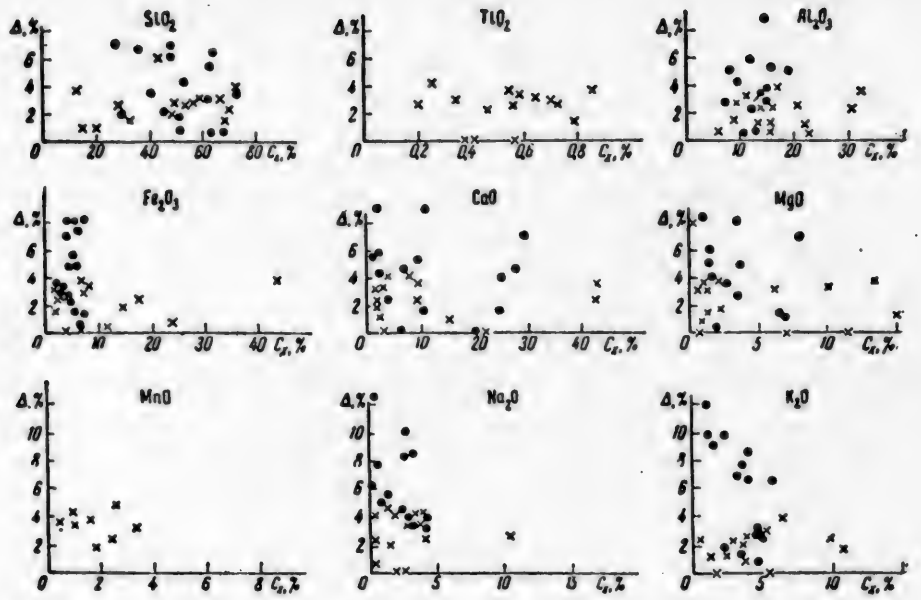

Fig. 9. Comparison of the results of spectrographic and chemical analysis of the main components of rocks:
C_x) the content of the metal oxides according to chemical analysis; Δ) the relative value of the deviation of the results of spectrographic determinations of element oxides by means of an impulse arc (+) and a d.c. arc (⊙), from results obtained by chemical analysis.

2. The technique developed for the quantitative spectrographic determination of Si, Ti, Al, Fe, Ca, Mg, Mn, Na, K in silicate rocks, does not require high dilution of the samples with cupric oxide and carbon powder for carrying it out. The mean arithmetic error for the determination of elements by this method is 2 — 3%.

The maximum deviation between the results of spectrographic and chemical analyses does not exceed 4%.

LITERATURE CITED

[1] I. V. Granovskii and N. P. Kuz'mina, Bull. Acad. Sci. USSR, Phys. Series, 18, 285 (1954).

[2] O. I. Nikitina, Bull. Acad. Sci. USSR, Phys. Series, 18, 285 (1954).

[3] E. E. Vainshtein, T. F. Borovik-Romanova and V. V. Korolev, J. Anal. Chem. 10, 158 (1955).*

[4] Iu. A. Makhnev, V. A. Stlanov and A. M. Shavrin, Bull. Acad. Sci. USSR, Phys. Series, 18, 272 (1954).

[5] S. Landergren and W. Muld, Mickrochimica acta 245 (1955).

[6] P. F. Lokhov, G. A. Kliushin and M. K. Volkova, Indust. Lab. 23, 579 (1957).

[7] B. J. Stallwood, J. Opt. Soc. America 44, 171 (1954).

[8] J. E. Hawley and Graham MacDonald, Geochimica et cosmochim. acta 10, 197 (1956).

[9] B. J. Rushton and G. D. Nicholis, Spectrochimica acta 9, 287 (1957).

[10] I. I. Levintov, Bull. Acad. Sci. USSR, Phys. Series, 9, 699 (1945).

[11] I. I. Levintov, Bull. Acad. Sci. USSR, Phys. Series, 11, 229 (1947).

[12] I. I. Levintov, J. Tech. Phys. 17, 781 (1947).

[13] I. I. Levintov, J. Tech. Phys. 17, 795 (1947).

* Original Russian pagination. See C.B. Translation.

[14] V. J. Caldecoustand J. Z. Saunderson, J. Opt. Soc. America 36, 99 (1946).

[15] E. I. Vorontsov, Indust. Lab. 19, 1180 (1953).

[16] A. N. Vorsin, Bull. Acad. Sci. USSR, Phys. Series, 18, 262 (1954).

[17] M. E. Britske, Bull. Acad. Sci. USSR, Phys. Series, 19, 58 (1955).

[18] N. N. Sobolev, J. Expt. Theor. Phys. 13, 131 (1943).

[19] N. N. Sobolev, J. Expt. Theor. Phys. 13, 137 (1943).

[20] O. M. Raiskii, J. Tech. Phys. 10, 431 (1940).

[21] E. Katz and L. Ornstein, Physica 4, 757 (1937).

[22] L. Ornstein and H. Brinkman, Physica 5, 145 (1938).

[23] H. Brinkman, Optische Stidie V. D. Lichtboog, Amsterdam, (1937).

[24] V. N. Kolesnikov and L. G. Fokhil'ko, Optics and Spectroscopy, 2, 689 (1957).

[25] E. E. Vainshtein and V. V. Korolev, J. Anal. Chem. 11, 627 (1956).*

[26] S. Kh. Kitaeva and V. V. Korolev, Paper Industry, 32, 4, (1957).

[27] A. K. Shubnikov, G. N. Soboleva, T. M. Bronovets and A. I. Khrisanova, Chemistry and Technology of Fuel and Oil, 10, 1 (1957).

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THE MUTUAL EFFECT OF ELEMENTS ON RADIATION INTENSITY IN A FLAME

COMMUNICATION I. THE USE OF THE TWO-SPRAYER TECHNIQUE

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Flame photometry has acquired considerable importance in recent years [1]. Descriptions of various types of apparatus have been published in which the requisite radiation is isolated by both light filters and by spectroscopes – monochromators. Numerous methods have been developed for analyzing a very wide variety of test materials – rocks, water, and industrial and biological materials. The method has found wide application for the determination mainly of the alkali and alkaline-earth metals, and also for a number of other elements.

During the determination of various metals it has been observed on several occasions that the results obtained depend to a very large extent on the composition of the solution, and on the presence of various impurities in the solution. The effect of foreign materials has been studied several times, and, despite the fact that the reason for this interference has not always been made sufficiently clear, nevertheless, practical techniques have been devised whereby determinations have been carried out with the required degree of accuracy. The mechanism of the effect of foreign materials can differ and depends on the nature of the material added, excitation conditions, and the properties of the radiating element. Of primary importance is the fact that interference during the determination of one element on the basis of the intensity of its spectral lines in the presence of another element, can be caused by the superposition of the molecular bands of the second element on the radiation of the first; thus the molecular band of SrOH is superimposed on the lithium line at 670.8 mμ. Another type of interference is connected with insufficient selectivity of the filters, and the transmission by the filters of part of the radiation from the foreign metals (for example, the light filter designed for the determination of sodium on the basis of the resonance doublet 589.0 – 589.6 mμ, usually, partly transmits the molecular band of CaOH with a maximum at 622 mμ, etc.). Interference is caused in spectrophotometers by the fact that the light is not sufficiently monochromatic, and by the presence of scattered light. We shall not go into any further discussion of the effect of interferences arising from the apparatus, nor of the effects caused by the action of organic materials which change the viscosity and surface tension of solutions, thereby affecting the spraying process, but we shall concentrate on the mutual effect of inorganic materials.

The Mutual Effect of the Alkali Metals on the Radiation. Lundergardh, who was the first to develop in detail the technique of working with a flame, was of the opinion that the alkali metals have very little effect on the intensity of one another [2]. However, more detailed studies by Borovik-Romanova [3] on rubidium, showed that the intensity of the rubidium line at 780.0 mμ is depressed in the presence of the chlorides of sodium and potassium, and in the presence of the bromide and iodide of these metals, but does not change in the presence of sodium fluoride. We shall discuss the explanation given by Mandel'shtam [4] for this phenomenon during a description of the "anion effect"; Mandel'shtam explained it by a decrease in the percentage dissociation of rubidium chloride in the flame.

Ivanov [5] has also observed a drop in the intensity of the rubidium line, when sodium chloride is present at the same time as rubidium in solution, nevertheless, this decrease was only observed when illuminating gas

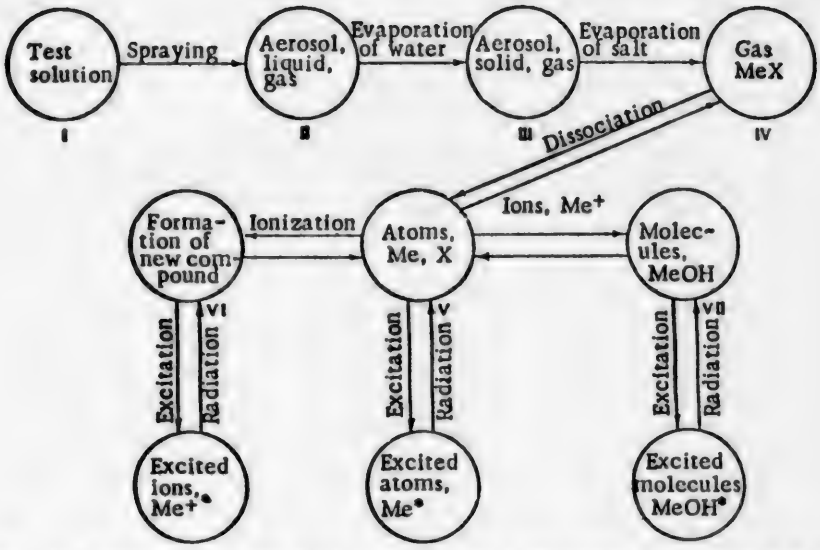

Fig. 1. Schematic diagram of processes which occur during introduction of a solution of a metal salt, MeX, into a flame.

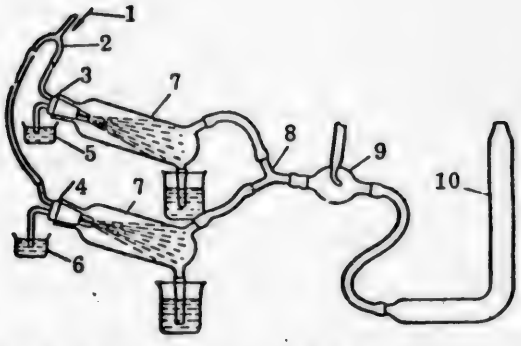

Fig. 2. Schematic diagram of the setup used for introducing solutions into the flame by means of two sprayers:
1) Compressed air supply; 2) T-piece; 3 and 4) sprayers; 5 and 6) test solutions; 7) sprayer chamber; 8) T-piece; 9) mixer for introduction of fuel gas; 10) burner.

was used (T. F. Borovik-Romanova used an acetone vapor flame, the temperature of which is approximately the same as that of illuminating gas). In a flame from a mixture of acetylene and air he observed strengthening of the rubidium lines. A study of the mutual effect of the alkali metals on powdered silicic acid containing metal salts, which was introduced into a flame, led to the important conclusion that the increase in radiation intensity is greater, the higher the atomic weight of the element added, and also the higher the atomic weight of the radiating element when the same impurity is present. Similar observations and conclusions have been made by Putzmann [6]. Subsequently, the mutual increase in the radiation of the alkali metals — mainly sodium and potassium — has been observed on many occassions [7 — 12], and is, at present, explained on the basis of the ionization processes of the metal atoms in the flame.

According to this explanation, during ionization of the metal in the flame gases according to the equation

$$Me \rightleftarrows Me^+ + e^- \quad (e^- \text{ — electron})$$

there exists an equilibrium between atoms, ions, and electrons:

$$\frac{P_{Me^+} \cdot P_{e^-}}{P_{Me}} = K$$

TABLE 1

Experiments Carried Out With Two Sprayers on Readily Ionizable Metals (air-acetylene flame)

Test element and its concentration in solution		λ in mμ	Element added, and its concentration, in γ/ml	Photocurrent value on addition of the foreign element into the flame (as a % of the photocurrent obtained in the absence of the foreign element)	
γ/ml	M			taken together	taken separately
Cs, 26.6	$2 \cdot 10^{-4}$	852	K 50	407	445
Cs, 26.6	$2 \cdot 10^{-4}$	852	K 100	617	622
Cs, 26.6	$2 \cdot 10^{-4}$	852	K 500	1416	1330
Cs, 26.6	$2 \cdot 10^{-4}$	852	K 1000	1520	1460
Cs, 50	$3.75 \cdot 10^{-4}$	852	K 1000	834	783
Cs, 100	$7.5 \cdot 10^{-4}$	852	K 1000	563	590
K, 3.9	10^{-4}	766 – 769	Cs 133	863	800
K, 9.8	$2.5 \cdot 10^{-4}$	766 – 769	Cs 133	469	483
K, 19.5	$5 \cdot 10^{-4}$	766 – 769	Cs 133	380	379
K, 39	$10 \cdot 10^{-4}$	766 – 769	Cs 133	253	253

(Saha's equation [13, 14] P_{Me}, P_{Me^+}, P_{e^-} are the partial pressures of the atoms, ions, and electrons).

On introducing another ionizing metal into the flame, the partial pressure P_{e^-} of the electrons increases, as a result of which the partial pressure of the ions should decrease, while P_{Me} should increase.

This assumption does,in fact,explain fairly well all the regularities involved in the mutual increase in intensity of the alkali metals in a flame, such as: the fact that the effect is observed to a greater extent in hotter flames and for metals which have low ionization potentials, the fact that the effect is observed to a greater extent at low concentrations,the fact that the greatest effect is observed on introducing readily ionizable metals (cesium), the fact that this increase in intensity of the radiation of a metal proceeds only to a certain limit, which corresponds to suppression of ionization, and, finally explains the linear relationship which exists between radiation intensity and concentration in the presence of another alkali metal.

The Anion Effect. The change in percentage dissociation of metal salts on introducing large amounts of salts of other metals, according to Mandel'shtam [4], is the reason for the drop in intensity of the radiation of thealkali metals. Dissociation of a metal halide according to the equation MeX⇌Me + X (X – halide) should conform to the law of mass action:

$$\frac{P_{Me} \cdot P_X}{P_{MeX}} = K,$$

where P_{Me}, P_X, P_{MeX} are the partial pressures of the metal atoms, the halide, and the salt respectively. The addition of more atoms of halide which increases P_X should lead to a decrease in P_{Me}, and this, in turn, should lead to a drop in the intensity of the radiation of the element in the flame. In such cases, a similar effect should be exhibited not only by salts of the alkali metals, but also by acids and their ammonium salts. Experimental confirmation of this is to be found in [15]. Another possible explanation is the effect of acids or their salts on the evaporation of the solvent from drops of aerosol during its passage through the chamber of the sprayer; this affects the amount of material reaching the flame without deposition on the chamber walls [16].

The effect of acids depends on their nature and their concentration, and is most strongly expressed in the case of phosphoric acid. It has been established that with increasing phosphoric acid concentration up to a cer-

TABLE 2

Investigation of the Nature of the Anion Effect

Test element and its concentration in solution		λ in mμ	Material added and its concentration, M	Photocurrent value on addition of the foreign material as a % of the photocurrent for the solution without addition of foreign material			
				Acetylene flame		Illuminating gas flame	
γ/ml	M			taken together	taken separately	taken together	taken separately
Na, 23	10^{-3}	589—589,6	HCl, 0,1	97	102	96,5	97
Na, 23	10^{-3}	589—589,6	HCl, 1,0	92	97	96	99
Na, 23	10^{-3}	589—589,6	HCl, 2,0	83,5	88	85	96
Na, 23	10^{-3}	589—589,6	HCl, 5,0	65,5	81	55,5	81,5
Na, 50	$2{,}2\cdot10^{-3}$	589—589,6	HCl, 5,0	55	66	—	—
K, 50	$1{\cdot}3\cdot10^{-3}$	766—769	HCl, 2,0	85	85	—	—
K, 50	$1{\cdot}3\cdot10^{-3}$	766—769	HCl, 5,0	56	81	—	—
K, 50	$1{\cdot}3\cdot10^{-3}$	766—769	2,0	86	91	—	—
Ca, 50	$1{,}25\cdot10^{-3}$	422,7	HCl, 5,0	55	66	—	—
Na, 23	10^{-3}	589—589,6	NH_4Cl 1,0	84	90	78	87
Na, 23	10^{-3}	589—589,6	NH_4Cl 2,0	79	88	77	88
Na, 23	10^{-3}	589—589,6	NH_4Cl 5,0	55	75	55	78

TABLE 3

The Effect of Sulfuric and Phosphoric Acids on the Radiation Intensity of the Alkali Metals

The test element and its concentration in solution		λ in mμ	Material added and its concentration, in M	Value of the photocurrent on adding other material, as % of photocurrent of solution without addition of other material			
				Acetylene flame		Illuminating gas flame	
γ/ml	M			together	separately	together	separately
K,50	$1{,}3\cdot10^{-3}$	766—769	H_2SO_4, 0,5	84	100	—	—
Na,23	10^{-3}	589—589,6	H_2SO_4, 0,5	96	96	90	96
Na,23	10^{-3}	589—589,6	H_2SO_4, 2,0	73	93	65	92
Na,50	$2{,}2\cdot10^{-3}$	589—589,6	H_2SO_4, 1,0	75	93	—	—
K,50	$1{,}3\cdot10^{-3}$	766—769	H_3PO_4, 2,0	39	53	—	—
K,39	$1\cdot10^{-3}$	766—769	H_3PO_4, 0,1	82	87	68	68
K,39	$1\cdot10^{-3}$	766—769	H_3PO_4, 1,0	48	57	24	30,6
Na,23	$1\cdot10^{-3}$	589—589,6	H_3PO_4, 0,1	90	95	98	98
Na,23	$1\cdot10^{-3}$	589—589,6	H_3PO_4, 1,0	66	82	57	71

TABLE 4

Effect of Phosphates on the Radiation Intensity of Calcium

Ca concentration		λ in mμ	Concentration of $(NH_4)_2HPO_4$, in M	Value of photocurrent on addition of other material, as % of photocurrent of original solution			
				Acetylene flame		Illuminating gas flame	
γ/ml	M			taken together	taken separately	taken together	taken separately
100	$2{,}5\cdot10^{-3}$	622	$1{,}65\cdot10^{-3}$	65	100	—	—
100	$2{,}5\cdot10^{-3}$	422,7	$1{,}65\cdot10^{-3}$	65	100	—	—
100	$2{,}5\cdot10^{-3}$	622	$1{,}65\cdot10^{-3}$	—	—	13	98
40	$1\cdot10^{-3}$	422,7	$0{,}66\cdot10^{-3}$	73	99	—	—
40	$1\cdot10^{-3}$	622	$0{,}66\cdot10^{-3}$	—	—	14,2	97
20	$5\cdot10^{-4}$	422,7	$3{,}3\cdot10^{-4}$	85,5	100	—	—
20	$5\cdot10^{-4}$	622	$3{,}3\cdot10^{-4}$	—	—	16	95

tain limit, there is a drop in the intensity of calcium radiation; beyond this limit phosphoric acid does not exhibit a quenching effect [17]. Quantitative results testify to the formation of compounds between phosphorus and calcium with ratios of Ca:P = 1:1, 3:2 [18, 19] or even 2:1 [20].

Formation of Compounds between Metal Oxides. A detailed study has been made of the quenching of the radiation of alkaline earth metals in the presence of aluminum salts [17]. At a sufficiently high concentration of aluminum salts, the radiation of the alkaline earth metals can be suppressed completely; this opens up new possibilities for the determination of traces of alkali metals in the presence of the alkaline earths [21, 22]. One suggestion advanced to explain the quenching effect of aluminum on calcium radiation is the formation of stable, sparingly volatile compounds with low thermal conductivity [22], for example $CaAl_2O_4$ [23], which does not succeed in evaporating during its passage through the flame [24].

A Study of the Mechanism of the Effect of Foreign Materials on the Radiation Intensity of the Elements in a Flame. The mechanism of the effect of a material on the radiation intensity of elements in a flame may differ in different cases. For further discussion it is useful to consider the processes which occur on introducing a solution of the salt of an element MeX into a flame (Fig. 1).

The test solution (I) after passing out of the sprayer forms an aerosol consisting of fine drops of solution (II), which, initially, as the result of evaporation of water in the flame, is converted into an aerosol consisting of solid particles of salt (III). When the salt evaporates, a gas MeX (IV) is formed, this being in equilibrium with the dissociation products, atoms of Me and X (V). The atomic gas ionizes partially to give, initially, Me^+ ions (VI), which partially form new compounds with molecules and radicals, for example MeOH (VII). The radiation of the resonance lines is determined by the partial pressure of the metal atoms, while every change in the preceding processes (I – IV) or in those processes occurring in parallel (ionization, formation of hydroxides) will affect the radiation intensity.

A foreign material, contained in the test solution, may depress the radiation intensity of the metal as a result of its action on one of the processes shown in the schematic diagram, since they are all responsible for the partial pressure of the atomic gas or that of the ions and the hydroxide molecules. Which of these processes is affected can be established by using various techniques, for example by measuring the ionization of the flame it can be established whether this process is affected, or, by measuring separately the intensity of the radiation of the atoms, molecules, and ions, it can be established whether changes occur in the formation of new compounds or ions. In the present article, we shall deal with results obtained on introducing the foreign material and a solution of a salt of the test element into the flame separately.

Such a technique permits one to establish whether it is the processes which the atomic gas undergoes, or the preceding processes (spraying, evaporation, and dissociation) which break down.

Technique and Experimental Results. In order to introduce the foreign material separately into the flame, a burner was constructed which was fed from two sprayers (Fig. 2); the spraying efficiency of these sprayers was the same. The burner was fitted in front of the inlet slit of a type UM-2 spectroscope-monochromator; the width of the monochromator slit was 0.1 mm. The light from the outlet slit of the monochromator was focussed by means of a UF-153 lens onto the cathode of a FEU-19 or FEU-22 photomultiplier, for carrying out measurements in the visible and infrared parts of the spectrum respectively. The photomultiplier was fed from a stabilized high-voltage rectifier, permitting smooth changes in voltage up to 2000 volts. A mirror galvanometer with a sensitivity of 5×10^{-9} a/mm of the scale was connected into the anode circuit of the FEU through a voltage divider – sensitivity regulator. The pressure of the compressed air, supplied by a compressor, was measured by a metal manometer, while the pressure of the acetylene was regulated by a reducer, followed by a screw-clip for accurate adjustment; the pressure was finally measured by means of a water manometer. Illuminating gas was taken from the city supply.

In order to study the mechanism of the action of a material on the radiation intensity of any element, solutions of definite concentrations were prepared; they included: solutions of a salt of the test element, and of the foreign element taken separately, and solutions of salts of the test element and foreign element taken together. These solutions were fed into the flame through two sprayers in the following order: the solution of a salt of the test element (left sprayer) – water (right sprayer); the solution of a salt of the test element (left sprayer) – the solution of a salt of the foreign element (right sprayer); the solution of the salts of the test element and foreign element (left sprayer) – water (right sprayer).

TABLE 5

Effect of Aluminum Salts on the Radiation Intensity of Calcium and Strontium

Taken		λ in mμ	Concentration of $Al(NO_3)_3$, in M	Value of the photocurrent of the solution obtained on addition of aluminum nitrate as a % of the photocurrent of the original solution			
				Acetylene flame		Illuminating gas flame	
γ/ml	mole/liter			taken together	taken separately	taken together	taken separately
Ca, 40	10^{-3}	422.7	$2 \cdot 10^{-3}$	30	99	—	—
Ca, 40	10^{-3}	622	$2 \cdot 10^{-3}$	30	99.5	23	100
Ca, 100	$2.5 \cdot 10^{-3}$	422	$5 \cdot 10^{-3}$	31	100	—	—
Ca, 100	$2.5 \cdot 10^{-3}$	622	$5 \cdot 10^{-3}$	30	100	38	98
Sr, 88	10^{-3}	460.8	$2 \cdot 10^{-3}$	35	100	10	98
Sr, 88	10^{-3}	680	$2 \cdot 10^{-3}$	36	100	15	100
Sr, 220	$2.5 \cdot 10^{-3}$	460.8	$5 \cdot 10^{-3}$	31	100	18	97
Sr, 220	$2.5 \cdot 10^{-3}$	680	$5 \cdot 10^{-3}$	31	100	14	95

When the monochromator is adjusted to isolate the lines or the bands of the test element, the readings obtained for the photocurrent in the second case (test element and foreign element taken separately), and in the third case (test element and foreign element taken together) are expressed as percentages of the readings obtained in the first case for the solution of test element alone.

Table 1 contains results obtained with the two sprayers on using readily ionizable metals — cesium and potassium. These experiments were carried out at low concentrations of the test element, at which the effect of ionization is most strongly expressed; only an acetylene flame was used, since it is in this flame that the effect is most pronounced.

The increase in the intensity of the radiation of cesium and potassium differs for differing concentrations of cesium and of the alkali metal added; the intensity decreases with increasing concentration of the main metal and increases with increasing concentration of the element which quenches the ionization. Of essential importance, however, is the fact that the increase in the radiation is almost or exactly the same whether the foreign element is added in solution or from outside; this confirms the assumption regarding the interaction of the alkali metals in the gaseous state.

Table 2 contains the results of experiments on the study of the nature of the "anion effect" in the case of hydrochloric acid and ammonium chloride. The concentration of these materials taken is relatively high in view of their weak effect on the radiation intensity of the elements. Experiments were carried out with acetylene and illuminating gas flames respectively.

Both hydrochloric acid and ammonium chloride act, presumably, by preventing evaporation of the metal, and, in addition, by reacting in the flame gases with the metal. The existence of such a combined effect is testified to by the drop in the radiation intensity which occurs on introducing the other material into the flame both in the same solution as the test element, or through the other sprayer; the drop is, however, greater in the first case.

The effect of sulfuric and phosphoric acids on the radiation intensity of the alkali metals is observed in the results given in Table 3.

Sulfuric acid, in the main, prevents evaporation from aerosol particles, since it has almost no effect on the radiation of potassium and sodium on introducing it separately; phosphoric acid; obviously exhibits the combined effect, since it forms compounds with the alkali metals in the flame, and also prevents evaporation or spraying the latter is especially marked for high concentrations of phosphoric acid.

Table 4 contains results of experiments carried out to establish the way in which phosphate affects the

intensity of calcium radiation. The phosphate concentration was two thirds of the calcium concentration in each case.

When phosphate solution was introduced separately into the flame it had absolutely no effect on the radiation intensity of calcium; when, however, the phosphate was the same solution as the calcium it did depress the calcium radiation intensity. Since at low phosphate concentrations, a break down of the spraying processes could not occur,the surface tension and the specific gravity of such solutions hardly differ at all from the corresponding values for pure water), then, obviously, evaporation of calcium from the aerosol particles is inhibited by the solid salt.

Assuming that compounds are formed between phosphorus and calcium in the flame, it can be postulated that these compounds are formed at the moment of evaporation of the solvent from the drop of solution, and are characterized by low volatility.

Finally, Table 5 contains the results obtained during experiments carried out to explain the nature of the influence of aluminum salts on the radiation of calcium and strontium.

In this case again, as can be seen from Table 5, the effect of the aluminum salt is only manifested when the aluminum salt is present in the same solution as the alkaline earth metal salts; thus, aluminum, mainly, prevents evaporation of calcium and strontium from solid aerosol particles, while the mechanism of its action reduces to the formation of compounds with the alkaline earth metals at the moment of evaporation of drops of the aerosol in the flame.

Thus, by adopting the technique of separate introduction of materials into the flame, by using two sprayers supplying one burner, it is possible to obtain experimental confirmation of the mechanism suggested for the effect of foreign materials on the radiation intensity of elements in a flame.

SUMMARY

Using a setup with two sprayers feeding one flame,a study has been made of the mechanism of the influence of a series of materials on the radiation intensity of the alkali and alkaline earth elements in a flame. It has been confirmed that the mechanism of this influence differs in various cases.

LITERATURE CITED

[1] N. S. Poluektov, Indust. Lab. 21, 9, 1045 (1955).

[2] H. Lundergardh, Die Quantitative Spectralanalyse der Element, Jena, (1929).

[3] T. F. Borovik-Romanova, Proc. Acad. Sci. 21, 334 (1938).

[4] S. L. Mandel'shtam, Proc. Acad. Sci. 22, 407 (1939).

[5] D. N. Ivanov, Indust. Lab. 10, 401 (1941).

[6] H. Putzmann, Spectrochim. acta 1, 5, 408 (1940).

[7] W. Klyne, Spectrochim. acta 4, 64 (1950).

[8] L. Huldt, Thesis, Upsala, (1948).

[9] W. Schuhknecht, Optik 10, 6,271 (1953).

[10] P. Porter and G. Wyld, Analyt. Chem. 27, 5, 733 (1955).

[11] E. Pungor and E. Zapp, Acta chim. Acad. scient. hung; 7, 1-2, 185 (1955); P. Ref. Chem. II. (1956) 32754.

[12] D. L. Rothermel, Amer. Soc. Testing Materials, Techn. Publ. 116, 117 (1951).

[13] Saha, Proc. Roy Soc. A 99, 135 (1921).

[14] R. Mavrodineanu and H. Boiteaux, L'analyse spectrale quantitative par la flamme, Paris, (1954).

[15] G. Collins and H. Polkinhorne, Analyst 77, 8,430 (1952).

[16] F. Eggertsen, G. Wyld and Z. Lykken, Amer. Soc. Testing Materials, Techn. Publ. 116, 52 (1951).

[17] R. Mitchell and J. Robertson, J. Soc. Chem. Ind. 55, 263 (1936).

[18] L. Leyton, Analyst 79, 497 (1954).

[19] G. Baker and Z. Johnson, Analyt Chem. 26, 465 (1954).

[20] S. Tsuchihashi and E. Sekido, J. Chem. Soc., Japan. Pure chem. Sect. 77, 5, 708 (1956); Analyt. Abstrs. 4, 2, 755 (1957).

[21] J. Spector, Anal. Chem. 27, 9, 1452 (1955).

[22] W. Schunknecht and H. Schinkel, Z. analyt. Chem. 143, 321 (1954).

[23] D. N. Ivanov, J. Anal. Chem. 9, 344 (1954).

[24] M. Margoshes and B. Vallee, Analyt. Chem. 28, 2, 180 (1956).

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THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 3. THE PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF COPPER*

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Many photometric methods are known at present for the determination of copper. The most widely used methods have been described in textbooks and reviews [1 – 2]. For the determination of traces of copper the reagents most widely used are dithizone [3 – 8], and sodium diethyldithiocarbamate [9 – 11]. The drawback of both these reagents is the impossibility of using them for the determination of copper in the presence of bismuth. In the case of diethyldithiocarbamate, manganese, nickel, cobalt, and large amounts of iron also interfere with copper determination. Many other organic reagents and the photometric methods which have been developed on their basis for the determination of copper, have not, hitherto, found wide application, either because they have not been examined sufficiently, or because the reagents are not readily available.

Peive and Ivanova [12] have used thiooxine (8-mercaptoquinoline) – which we have suggested – for the rapid, direct photometric determination of copper in soils without preliminary removal of iron and manganese. In the present article the effect of other elements on the accuracy of copper determination is considered, together with the limits of applicability of the method.

Thiooxine in neutral, acid, and alkaline solutions, forms with cupric ions a dark-brown salt $Cu(C_9H_6NS)_2 \cdot {}^1/_2H_2O$ which is insoluble in water.

Found %: Cu – 15.81; S – 15.97; N – 6.90; H_{active} – 0.28

Calculated %: Cu – 16.18; S – 16.29; N – 7.12; H_{active} – 0.25

The amount of water of crystallization in cupric thiooxinate was determined by the method for the determination of active hydrogen of Chugaev – Zerevitinov [13], rather than by drying (because of the possible danger of oxidizing the complex). The copper complex was dried for analysis in a vacuum at 14 deg. It is possible that some of the water of crystallization may be lost under these conditions, and that in actual fact cupric thiooxinate contains a whole molecule of water of crystallization and not half a molecule.

Cupric thiooxinate is readily extracted by chlorobenzene, bromobenzene, chloroform, amyl acetate, isopropanol; it is not extracted so readily by benzene, toluene, xylene, dichloroethane; and is only very poorly extracted by carbon tetrachloride, carbon disulfide, and is completely insoluble in aliphatic hydrocarbons.

Cupric thiooxinate is completely extracted from both alkaline and acid solutions (Fig. 1).

In order to take its absorption spectrum, cupric thiooxinate was prepared by adding a solution of Cu^{2+} (1:1000) to excess of an acid (pH 1) solution of thiooxine. The brown precipitate which separated out was filtered off, and washed with water, alcohol, and ether, and finally dried. An aliquot of the complex was dissolved in chloroform and its spectrum registered on a SF-4 spectrophotometer. As shown in Fig. 2, the absorption spectrum of cupric thiooxinate has three maxima: the first lies at 252.5 mμ, the second at 275 mμ, and the third in the

* Communication 2, see J. Anal. Chem. 13, 507 (1958).

visible spectrum at 431 mμ. The corresponding molar extinction coefficients are: at λ_1=252.5 mμ, ϵ_1=31000; λ_2=275 mμ, ϵ_2=29000; λ_3=431 mμ, ϵ =7530.

Conformity to Beer's law was studied in the usual way by extracting cupric thiooxinate from 2.5 N HCl at a thiooxine concentration of 0.25 g in 50 ml of solution. As the curve in Fig. 3 shows, the calibration curve is linear up to 8 γ of copper in 1 ml of chloroform.

Thiooxine, like all organic reagents of the type R − SH, according to current theoretical ideas, should interact in aqueous solutions only with those elements which form sulfides which are stable towards water. In this connection, even very high concentrations of the alkali, and alkaline earth metals, and also Al, Ti, Zr, Th, Hf, Cr, etc, do not interfere with the determination of copper. In addition to copper, Pd, Ru, Os, Pt, Ag, Au, Hg, Mo, and W also react with thiooxine in strongly acid solutions. The first three elements should therefore be absent; platinum can be tolerated up to about 50 γ. Silver, mercury, and gold form thiooxinates which are not extracted by organic solvents. Silver (even in amounts of 50 γ) interferes with copper determination, presumably as a result of coprecipitation of copper with the very stable silver thiooxinate. The thiooxinates of divalent mercury and trivalent gold do not coprecipitate cupric thiooxinate, and moderate amounts of Hg^{2+} and Au^{3+} (4 and 10 mg respectively) do not interfere with copper determination.

Molybdenum forms a complex, $MoO_2(C_9H_6NS)_2H_2O$, with thiooxine, and, in acid solutions, the stability of this complex is similar to that of cupric thiooxinate. Molybdenum present in amounts of 5 − 10 γ in the test solution can be masked by 0.5 − 1 g of ammonium thiocyanate. Tungsten thiooxinate is insoluble in chloroform and does not interfere with the determination of copper.

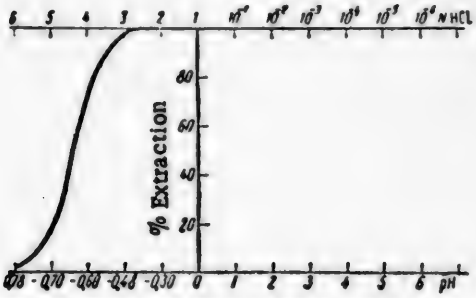

Fig. 1. Extractability of cupric thiooxinate as a function of the reaction of the medium.

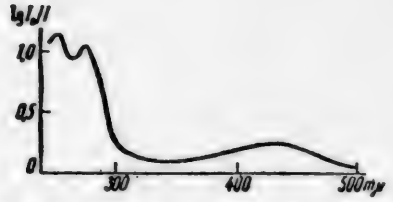

Fig. 2. Absorption spectrum of a 0.000036 M solution of cupric thiooxinate in chloroform.

Very large amounts of tungsten can be kept in solution by means of oxalic acid.

Antimony in amounts greater than 50 γ leads to high results for copper (40 γ).

What is essential is that considerably preponderant amounts of bismuth (which interferes with copper determination by means of the dithizone and diethyldithiocarbamate methods) do not interfere with copper determination by means of thiooxinate.

The effect of other elements on the accuracy of copper determination is shown in the Table.

Both in 2.5 N HCl media, and in weakly acid and alkaline solutions, high concentrations of the common anions (chloride, bromide, fluoride, sulfate, tartrate, oxalate, etc.) do not affect the accuracy of copper determination. In alkaline media, cyanide, when present in an appreciable excess, interferes with complete extraction of copper.

Analytical Procedure. To 15 − 20 ml of a weakly acid (pH 3 − 5) test solution contained in a separating funnel is added 5 ml of a 10% solution of ascorbic acid, followed by 10 ml of a 20% solution of potassium hypophosphite (acidified with hydrochloric acid to the methyl orange end point), 10 ml of a saturated solution of oxalic acid, and 10 ml of concentrated hydrochloric acid (sp. gr. 1.18). The contents of the funnel are shaken, and

TABLE

Determination of Copper in the Presence of Foreign Elements (30 γ Cu taken)

Foreign element (Me), in mg	Ratio Cu : Me	Cu found, in γ	Foreign element (Me), in mg	Ratio Cu : Me	Cu found, in γ
Fe^{II} — 40	1 : 2000	32	Sn^{II} — 10	1 : 500	28
Zn — 10	1 : 500	30	Mn^{II} — 28	1 : 1400	31
Cd — 100	1 : 5000	31	Pb — 10	1 : 500	31
Co^{II} — 5	1 : 250	29	Tl^{I} — 100	1 : 5000	30
Ni — 8	1 : 400	29	As^{V} — 200	1 : 10000	30
W^{VI} — 50	1 : 2500	30	As^{III} — 10	1 : 500	32
Bi^{III} — 6	1 : 300	28	Ge — 50	1 : 2500	31
Sb^{III} — 0,05	1 : 2,5	29	Hg^{II} — 4	1 : 200	28
V^{IV} — 80	1 : 4000	31	U^{VI} — 50	1 : 250	32
Se^{IV} — 10	1 : 500				

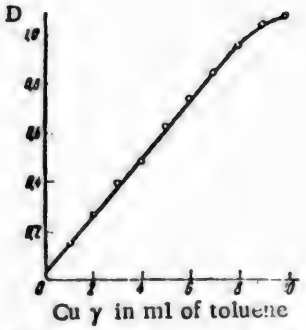

Fig. 3. Conformity to Beer's law of a solution of thioxinate in toluene (filter S-47).

then dropwise, with shaking, is added 5 ml of reagent solution (5 g of the potassium salt of thiooxinate is dissolved in 77 ml of water and 23 ml of concentrated hydrochloric acid added; a transparent yellow-orange solution is thereby obtained which is stable in a closed vessel for several weeks). After 2 — 3 minutes, 10 ml of toluene or xylene is added and the contents shaken vigorously for 3 — 4 minutes to extract the cupric thiooxinate. The extract is removed and filtered through a plug of cotton wool; photometric measurements are made on the filrate at 431 mμ, or by means of a S - 42, or S - 47 filter; the copper content is then determined from a calibration curve constructed by means of pure solutions of copper using all the reagents listed above.

SUMMARY

1. The interaction of thiooxine (8-mercaptoquinoline) with copper in various media, in the presence of foreign cations, has been studied.

2. Cupric thiooxinate $Cu(C_9H_6NS)_2 \cdot {}^1/_2H_2O$ is stable in strongly acid solutions and is readily extracted by many organic solvents to give solutions with an intense brown color.

3. A photometric method has been developed for the determination of traces of copper (3 — 30 γ) in the presence of predominating amounts of bismuth, manganese, iron, nickel, and other elements.

LITERATURE CITED

[1] V. N. Podchainova, "Methods of Determining Copper," [in Russian] Metallurgizdat, Sverdlovsk — Moscow, (1947).

[2] F. Snell, Colorimetric Methods of Analysis, 2 (1948).

[3] H. Fischer and G. Leopoldi, Wiss. Veröffentlich. Siemens-Konzern 12, 44 — 52 (1933); Angew. Chem. 47, 90 (1934).

[4] G. Schwarz, O. Fischer and H. Stotz, Milchwirtschaft. Forsch. 17, 314 (1936); 18, 196 (1936).

[5] E. B. Sandel, Ind. Eng. Chem., Anal. Ed. 9, 464 (1937).

[6] S. Schweibold, B. Bleyer and G. Nagel, Biochem. Z. 297, 324 (1938).

[7] A. K. Babko and A. T. Pilipenko, J. Anal. Chem. 1, 275 (1946); 2, 33 (1947); 5, 14 (1950).

[8] R. Alekseev, Zavod. Lab. 415 (1938); N. S. Kuziagina, Zavod. Lab. 8, 174 (1939).

[9] T. Gallan and S. Russel, Analyst 54, 650 (1929).

[10] M. Piccotti and G. Buldossi, Microchemie 30, 77 (1942).

[11] C. Greenleaf, J. Assoc. Official Agr. Chem. 25, 305 (1942).

[12] Ia. V. Peive and N. N. Ivanova, Agriculture, No. 11, 4 (1953).

[13] L. Gatterman and G. Willand, "Practical Work in Organic Chemistry", Goskhimizdat, Moscow — Leningrad, (1948) [In Russian].

DIALKYL- AND DIARYLDITHIOPHOSPHORIC ACIDS AS ANALYTICAL REAGENTS

COMMUNICATION 7. AMPEROMETRIC AND VISUAL TITRATION OF LEAD BY MEANS OF NICKEL DIETHYLDITHIOPHOSPHATE, IN THE PRESENCE OF BARIUM, CALCIUM, ZINC, AND OTHER ELEMENTS*

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Ions of a number of heavy metals, under certain conditions, are almost quantitatively precipitated as compounds with a constant composition by means of solutions of dialkyl- and diaryldithiophosphoric acids. The precipitates separate out, even from very dilute solutions, at a fairly rapid rate. This fact permits one to develop, on the basis of the precipitation reaction, amperometric, visual, and other titrimetric methods of determining certain elements.

Anions of dialkyl- and diaryldithiophosphoric acids are not reduced on the dropping mercury cathode or on the rotating platinum microcathode. Accordingly, amperometric titration based on the cathode current can only be realized for those ions which are reduced on the electrodes indicated.

Recently [1] it was established that anions of diaryldithiophosphoric acids are oxidized on a dropping mercury anode and on a rotating platinum microanode; a linear relation exists between the current and concentration of dialkyldithiophosphate (below 1 millimole/liter) in the case of oxidation on a dropping mercury anode. During electrolysis of a 10^{-3}M solution of sodium diethyldithiophosphate in 0.100 M perchloric acid, the half-wave potential is equal to -0.062 volt with respect to the saturated calomel electrode. Under these conditions, the following reactions occur on the dropping mercury electrode:

$$2Hg \rightarrow Hg_2^{2+} + 2e;$$
$$Hg_2^{2+} + {}^-SP(S)(OR)_2 \rightarrow Hg + Hg[SP(S)OR)_2]_2.$$

Thus, the mercury electrode does not behave as an inert electrode. The half-wave potential during oxidation of dialkyldithiophosphates on a dropping mercury electrode becomes more negative with increasing molecular weight of the radical, presumably as a result of a decrease in the solubility of the corresponding mercury dialkyldithiophosphates. The following reaction takes place on a platinum microanode:

$$2^-SP(S)(OR)_2 \rightarrow (RO)_2P(S)SS(S)P(OR)_2 + 2e.$$

The half-wave potential during electrolysis of a 10^{-3}M solution of sodium diethyldithiophosphate in 0.100 M perchloric acid on a rotating platinum microanode, is equal to +0.696 volt with respect to the saturated calomel electrode.

As an example of the use of a dialkyldithiophosphate for amperometric titration, a description is given in

*For Communication 6, see Bull. Moscow State University, 2, 1958, p. 177.

the present article of the amperometric titration of lead ions by means of nickel diethyldithiophosphate, using a rotating platinum microanode at a potential of +0.8 volt with respect to the saturated calomel electrode. In addition, it is also shown that, under certain conditions, lead can be titrated visually.

It has been pointed out before [2] that lead ions can be quantitatively precipitated by diethyldithiophosphoric acid from neutral and weakly acid solutions.* Under similar conditions the following ions are also precipitated: Hg^{2+}, Ag^{+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, Pd^{2+}, Pt^{II}, Ir^{III}, Rh^{III}, Sn^{II}, Sb^{III}, As^{III} (3 N HCl); while the following ions are not precipitated: K^{+}, Na^{+}, NH_4^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Be^{2+}, Al^{3+}, Zn^{2+}, Ge^{IV}, Cr^{III}, Mn^{2+}, Fe^{2+}, Ga^{3+}, Th^{4+}, V^{V}, U^{VI}. By using complexing agents and regulating the pH, the selectivity of diethyldithiophosphoric acid as a precipitant for lead can be increased.

Lead diethyldithiophosphate is a white, fine-crystalline material with a melting point of 74 deg; it is insoluble in dilute nitric acid, but is soluble in solutions of alkalis, ammonium acetate, and in a number of organic solvents. The sensitivity of detection of lead in weakly acid solutions is expressed by a limit of identification of 2 γ of Pb and a limiting dilution of 1:500,000.

According to published results [4 – 6], the composition of lead diethyldithiophosphate corresponds to the formula $[(C_2H_5O)_2PSS]_2Pb$. The results of our amperometric titration confirmed this formula. The latter was also confirmed by visual titration of a solution of lead nitrate with nickel diethyldithiophosphate to cessation of turbidity, and also by an iodometric method.

An approximate value for the solubility of lead diethyldithiophosphate was determined as follows. A freshly prepared and carefully washed precipitate of lead diethyldithiophosphate was periodically shaken with water for 24 hours at 22 – 24 deg. A known volume (20 – 60 ml) of the saturated solution which had been filtered through a fine filter paper was then transferred to a separating funnel, and excess bismuth nitrate (T_{Bi} = 0.001) added; the bismuth diethyldithiophosphate formed according to the reaction

$$2Bi(NO_3)_3 + 3[(C_2H_5O)_2PSS]_2Pb = 2[(C_2H_5O)_2PSS]_3Bi + 3Pb(NO_3)_2$$

was then extracted with 10 ml of carbon tetrachloride. The extraction was repeated. The yellowish extract was filtered into a 25 ml standard flask and the volume of the solution made up to the mark with carbon tetrachloride; the color of this solution was then measured photometrically on a SF-4 spectrophotometer at 400 mμ (one of the absorption maxima of bismuth) in a 10.01 mm cell, using carbon tetrachloride as the reference liquid. The amount of bismuth diethyldithiophosphate was determined from a calibration curve constructed beforehand using standard bismuth nitrate solution; the solubility of the lead diethyldithiophosphate was then calculated.

The solubility of lead diethyldithiophosphate in water proved to be 1.3×10^{-4} mole/liter (mean of three results near to each other).

The solubility product

$$L_p[(C_2H_5O)_2PSS]_2Pb = 8.6 \cdot 10^{-12}.$$

Qualitative tests showed that lead diethyldithiophosphate is less soluble than lead sulfate but more soluble than lead chromate.**

All that has been said above gives a basis for assuming that precipitation of lead as its diethyldithiophosphate should be suitable for developing an amperometric method for its determination. Certain properties of the lead diethyldithiophosphate formed also permit development of a visual method of titrating lead. Of the greatest practical interest is the possibility of carrying out amperometric and visual titration of lead in the presence of elements such as barium and calcium which are so difficult to separate from lead. These elements often occur together in a number of polymetallic ores, lead-calcium babbites, and lead-barium glass. Existing methods for the separation of lead from barium, strontium, and calcium [8] do not always give reliable results, and are characterized by the long time they take to carry out, and by the complexity of the procedures involved; in addition, they are not suitable for production control. During precipitation of lead by means of hydrogen sulfide from a dilute hydrochloric acid solution containing the alkaline earth metals, it is necessary to create conditions which exclude the formation of sulfuric acid anions (absence of strong oxidizing agents). Separation of

* Carius [3] was mistaken in his opinion that lead forms a water-soluble salt with diethyldithiophosphoric acid.

** Data on the solubility of lead sulfate and lead chromate can be found in the "Chemist's Notebook" [7].

TABLE 1

Amperometric Titration of Lead by Means of a Solution of Nickel Diethyldithiocarbamate

Lead taken		Metal added in the form of nitrate	Ratio Me/Pb	Amount of nickel diethyldithiophosphate sol. used, ml $N_{R_2Ni} = 0.02802$	Lead found	Error	
In ml	In g					In g	In %
0,5	0,00518	—	—	1,80	0,00522	+0,00004	+0,8
1	0,01036	—	—	3,50	0,01028	+0,00008	−0,8
3	0,03103	—	—	10,70	0,03103	−0,00005	−0,2
0,5	0,00518	0,12 K	25	1,75	0,00513	−0,00005	−1
1	0,01036	0,06 NH_4	6	3,50	0,01028	−0,00008	−0,8
1,5	0,01554	0,06 Co	4	5,30	0,01537	−0,00017	−1,1
1	0,01036	0,1 Ni	10	3,55	0,01030	−0,00006	−0,6
0,5	0,00518	0,15 Na	30	1,80	0,00522	−0,00004	−0,8
0,5	0,00518	0,027Cr	5	1,80	0,00522	−0,00004	−0,8
2	0,02072	0,038Mn	2	7,10	0,02061	−0,00011	−0,5
0,5	0,00518	0,065Mg	13	1,80	0,00522	−0,00004	−0,8
0,5	0,00518	0,015Al	3	1,80	0,00522	−0,00004	−0,8
1	0,01036	0,055Zn	5	3,50	0,01028	−0,00008	−0,8
0,5	0,00518	0,21 Sr	40	1,80	0,00522	−0,00004	−0,8
0,5	0,00518	0,25 Ba	50	1,80	0,00522	−0,00004	−0,8
0,5	0,00518	0,12 Ca	25	1,80	0,00522	−0,00004	−0,8

lead from barium, strontium, and calcium by treating their sulfates with ammonium acetate is not quantitative. When lead sulfate is dissolved in ammonium acetate in the presence of calcium and strontium sulfates, strontium sulfate partially dissolves, to the same extent as in the absence of lead sulfate [9]. Satisfactory results can be obtained during separation of lead from barium, strontium, calcium, and magnesium by its precipitation in the form of PbOHCl [10], PbOHBr [11], or PbOHI [11] and then weighing as $PbCrO_4$. Methods of separating lead from the alkaline earth elements by means of organic reagents have not been widely used in practice, mainly because these reagents are not readily available. Morachevskii Zvereva and Rabinovich [12] separated lead from barium by passing a solution in 0.5 N HCl through a column of the anion exchange resins PE-9, EDE-10, and EDE-10-P in the perchlorate form; under such conditions, the anionic complex of lead is completely absorbed by the anion exchange resin, while barium passes into the filtrate. Lead is extracted with water. Methods of determining lead in the presence of the alkaline earth elements are few. The most satisfactory results are obtained during deposition of lead on the anode in the form of its dioxide. This method is, however, not used very much in practice. Existing amperometric methods of titration [13, 14] either do not permit determination of lead in the presence of the alkaline earth elements at all, or yield insufficiently accurate results.

TABLE 2

Visual Titration of Lead with Nickel Diethyldithiophosphate Solution for Various Acid Concentrations (volume of lead nitrate solution − 5.0 ml)

Pb taken, in g	Acid added, in ml	Pb found, in g	Error	
			Absolute in mg	Relative, in %
0,0258	—	0,0256	−0,2	−0,8
0,0258	—	0,0257	−0,1	−0,4
0,0417	—	0,0421	+0,3	+1
0,0835	—	0,0828	−0,7	−0,8
0,0258	5 HNO_3, 2,5 *N*	0,0266	+0,6	+2,3*
0,0258	5 HNO_3, 1,5 *N*	0,0260	+0,2	+0,8*
0,0258	5 HNO_3, 8 *N*	0,0257	−0,1	−0,4
0,0258	10 HCl, 0,1 *N*	0,0260	+0,2	+0,8

* In these experiments urea was not added.

Amperometric Titration of Lead with a Solution of Nickel Diethyldithiophosphate.* Amperometric titration was carried out on the usual setup with a rotating platinum microanode. The test solution containing 0.005 – 0.03 g of lead, and up to 0.25 g of barium, strontium, calcium, magnesium, zinc, iron and other elements of Group III, was titrated with 0.1 N nickel diethyldithiophosphate in a supporting electrolyte of 0.1 – 1 N HNO_3 at a potential of +0.8 volt for the platinum microanode with respect to the saturated calomel electrode. After the equivalence point has been reached, there is observed an increase in the diffusion current connected with oxidation of the anode by diethyldithiophosphoric acid to the disulfide.

The method gives satisfactory results (Table 1).

Mercury, silver, copper, cadmium and other heavy metals which form sparingly soluble diethyldithiophosphates interfere with determination of lead.

Visual Titration of Lead with a Solution of Nickel Diethyldithiophosphate. Where a setup for amperometric titration with a rotating platinum microelectrode is not available, lead can be determined quite satisfactorily by a visual method. On addition of nickel diethyldithiophosphate to a solution containing lead, a white turbidity develops, which, on shaking rapidly gives a flocculent, fine-crystalline precipitate; the mother liquor thereupon becomes completely transparent. Experiments have shown that it is quite easy to determine the end point on the basis of the cessation of turbidity on addition of one drop of nickel diethyldithiophosphate solution. Titration should be carried out in a wide, squat beaker placed on black paper. This facilitates establishment of the end point. Observations of the titration should be made from above. Near the equivalence point the beaker is shaken until the mother liquor is transparent. When large amounts of precipitate are formed, the beaker should be inclined so that the precipitate gathers in one place. Usually, a white, continuous film forms on the surface of the liquid being titrated; on addition of a drop of the reagent this film breaks up.

TABLE 3

Visual Titration of Lead with Nickel Diethyldithiophosphate in the Presence of Other Elements (initial volume of solution being titrated 15.0 ml)

Pb taken, in g	Salt added, in g	Ratio Me: : Pb	Pb found, in g	Error	
				Absolute, in mg	Relative, in %
0,0258	$2Ca(NO_3)_2 4H_2O$	13	0,0257	– 0,1	– 0,4
0,0516	$2Ca(NO_3)_2 4H_2O$	6,5	0,0515	– 0,1	– 0,2
0,0258	$1Sr(NO_3)_2$	15	0,0257	– 0,1	– 0,4
0,0258	$1Ba(NO_3)_2$	20	0,0257	– 0,1	– 0,4
0,0258	$1Ba(NO_3)_2$	20	0,0260	+ 0,2	+ 0,8
0,0774	$1Ba(NO_3)_2$	7	0,0773	– 0,1	– 0,1
0,0258	$1Zn(NO_3)_2 \cdot 6H_2O$	10	0,0257	– 0,1	– 0,4
0,0258	$1KNO_3$	15	0,0257	– 0,1	– 0,4
0,0258	$1Al(NO_3)_3 \cdot 9H_2O$	5	0,0260	+ 0,2	+ 0,8
0,0258	$1Mn(NO_3)_2 \cdot 6H_2O$	8	0,0257	– 0,2	– 0,4
0,0258	$1Ni(NO_3)_2 \cdot 6H_2O$	8	0,0260	+ 0,2	+ 0,8
0,0258	$1Co(NO_3)_2 \cdot 6H_2O$	8	0,0257	– 0,1	– 0,4
0,0516	$1Cr(NO_3)_3 \cdot 9H_2O$	5	0,0512	– 0,4	– 0,8
0,0258	$1Fe(NO_3)_3 \cdot 9H_2O$	5	0,0258	0	0
0,0516	$1Fe(NO_3)_3 \cdot 9H_2O$	2,5	0,0515	– 0,1	– 0,2

For facilitating observation of the formation of a turbidity in the mass of the solution, after addition of each new portion of titrant, the film formed on the surface is touched with the soaped tip of a glass rod; when this is done the film disappears.

The nickel diethyldithiophosphate solution is standardized by titration with an iodine solution or with a solution of lead nitrate obtained by dissolving a known amount of the chemically pure nitrate. In both cases, the same results are obtained.

The initial concentration of lead in the solution being titrated should be within the limits 0.01 – 0.1 mole/liter.

* Synthesis of nickel diethyldithiophosphate and preparation of its solutions have been described previously [2].

Changes in the nitric acid concentration over wide limits (0.01 – 4 N HNO_3) have almost no effect on the titration results for lead, as long as urea is added to the solution being titrated (Table 2).

Chloride ions, in small amounts, do not precipitate lead as the chloride, and do not interfere with the determination.

The visual method gives satisfactory results for the determination of lead in the presence of barium and other elements (Table 3), but takes a rather longer time than most titrimetric methods, and also requires some skill, and is applicable for the determination of relatively large amounts of lead.

The visual method of titrating lead is characterized by its simplicity, and is, probably, of equal value to the complexonometric method of determining lead in the presence of zinc [15].

Amperometric and visual titration of lead in the presence of the alkaline earth and other elements by means of nickel diethyldithiophosphate could be used for developing methods for the analysis of a number of polymetallic ores, lead-calcium babbites, and other materials.

SUMMARY

An amperometric method using a rotating platinum microanode at a potential of +0.8 volt, as well as a visual method of titrating lead with nickel diethyldithiophosphate solution have been developed for determining lead in the presence of the alkaline earth and many other elements. The methods give accurate results.

LITERATURE CITED

[1] R. F. Makens, H. H. Vaughan and R. R. Chelberg, Analyt. Chem. 27, 1062 (1955).

[2] A. I. Busev and M. I. Ivaniutin, J. Anal. Chem. 11, 523 (1956).*

[3] L. Carius, Lieb. Ann. 112, 190 (1859).

[4] P. S. Pishchimuka, J. Russ. Phys. Chem. Soc. 44, 1406 (1912).

[5] T. W. Mastin, G. R. Norman and E. A. Weilmuenster, J. Amer. Chem. Soc. 67, 1662 (1945).

[6] M. I. Kabachnik and T. A. Mastriukova, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 4, 731 (1952); No. 1, 123 (1953).*

[7] "Chemist's Notebook," (Edited by B. P. Nikol'skii), vol. III [in Russian] Goskhimizdat, Moscow – Leningrad, p. 84 (1952).

[8] W. F. Hillebrand, G. E. Lundell, H. A. Bright, and J. I. Hoffman, Applied Inorganic Analysis, [translated from English] Goskhimizdat, Moscow, 1957, p. 235, 236, etc..

[9] F. Feigl, Z. analyt. Chem. 84, 220 (1931).

[10] V. P. Shvedov, J. Gen. Chem. 17, 33 (1947).

[11] V. P. Shvedov, E. O. Gol'dshtein and N. I. Seletkova, J. Anal. Chem. 3, 109 (1948).

[12] Iu. V. Morachevskii, M. N. Zvereva and R. Sh. Rabinovich, Zav. Lab., 22, 541 (1956).

[13] H. A. Laitinen, Analyt. Chem. 21, 66 (1949); 24, 46 (1952); 28, 666 (1956).

[14] N. Konopik, Osterr. Chem. Z. 54, 289, 325 (1953).

[15] R. Pribil, "Complexones in Chemical Analysis," [Translated from Czech] IL, Moscow, p. 77 (1955).

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SPECTROGRAPHIC QUANTITATIVE DETERMINATION OF HAFNIUM IN ZIRCONIUM DIOXIDE

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Hafnium was discovered more than 30 years ago, but it is only in the last ten years that a number of important applications for this element have been found in modern industry. Very recently the demand arose for very pure zirconium [1]. In this connection, interest in both these elements increased sharply, and it became clear that in the overwhelming majority of cases these elements should be separated from each other as completely as possible.

The close similarity in the physical and chemical properties of hafnium and zirconium complicates the control of the degree of separation of these elements. Accordingly, development of simple and rapid analytical methods for mixtures of the oxides of Hf and Zr is very necessary. Spectrographic analysis is about the only method that would permit rapid and fairly accurate determination of the hafnium concentration of zirconium. The spectroscopist comes up against two characteristic properties in such an analysis. The zirconium spectrum consists of a very large number of lines, while in the hafnium spectrum, in the region available for analysis (2200 – 6000 A), there are no sensitive lines. Accordingly, even determination of as much as some thousandths of a percent of hafnium is by no means easy.

During the last ten years, several articles have been published on the spectrographic determination of hafnium in zirconium [2 – 7]. Only in one of these papers [2] is a method described for determination of thousandths of a percent of Hf. The remaining articles are devoted to samples in which the smallest amounts of hafnium come to hundredths or tenths of a percent.

Gusiatskaia and Rusanov [3] have published a very thorough study of the development of a technique for determination of Hf in Zr within the limits 0.1 to 65% during evaporation of the material from the canal of a carbon electrode in a d.c. arc. By means of additional results the lower limit of determination of hafnium can be lowered to some hundredths of a percent. This article contains a description of an original technique for exciting the Hf tablets from tablets obtained from mixtures of the sample with silver. The technique only requires economical expenditure of sample and permits determination of Hf within the limits 0.5 to 80%. According to the work of Kriuger and others [4] it is possible to determine Hf in amounts from 0.01% on evaporating the material from a carbon electrode.

The work of Kingsbury is very interesting [5].

For determing Hf within the concentration limits 0.01 to 55%, the test material is placed as a thin layer on the flat end of a graphite electrode and fixed there by means of a bakelite solution. The spectrum is excited in the discharge of a low-voltage spark. The standard error characterizing the experimental error is equal to 6%.

The present article contains a description of our work on the determination of hafnium oxide in zirconium oxide in the range of thousandths of a percent to several percent. In order to solve this problem two separate techniques have been developed which differ from those published earlier.

Determination of Low Concentrations of Hafnium Oxide. According to the results given in [2], a mixture of the test material with graphite and barium fluoride is burnt in the canal of a graphite electrode using a 30 amp. d.c. current. The spectra are registered on a spectrograph with a diffraction grating, and the Hf line at

2820.2 A is obtained at a HfO_2 concentration of 0.003%. Because we did not have an apparatus with a diffraction grating at our disposal, we used the KS-55, a prism spectrograph. As our experiments showed, when the spectra were excited under the conditions described in [2], it was found impossible to detect the hafnium line on the strong background when the amount of hafnium present was of the order of some thousandths of a percent.

In order to reduce the background, discontinuous exposure was used, while a totally different method of introducing the sample into the discharge was employed. 50 mg of the calcined and ground zirconium oxide was mixed in a mortar with 1 ml of glycerol for 4 minutes. A conical crater 1.5 mm deep was made in the lower electrode; the upper electrode was sharpened to a truncated cone. The electrodes were adjusted by shadow projection until the interelectrode gap was 3.5 mm, and, with the slit closed for 10 seconds, the a.c. arc switched on. The holder of the lower electrode was then withdrawn to the side and a drop of the glycerol suspension placed on the graphite by means of a pipet; the holder was then replaced in position. The glycerol evaporated rapidly and the test material in the form of a thin layer of powder was left securely on the electrode surface. Next, the slit was opened for 10 seconds while the arc was switched on, another drop of the suspension was then placed on the electrode. In all, 4 drops of suspension were placed on the electrode during a total exposure time of 40 seconds. The slit was illuminated with a three-lens system; the arc current used was 20 amperes. It was found essential to work at a definite rhythm. It was also found essential not to place the suspension on an electrode which was either too hot or too cold. In both extremes, loss of test material occurred.

The spectra were photographed on "Spectrographic Type II" plates with a sensitivity of 16 GOST units; the slit width was 0.01 mm. The developer used was special contrast developer D-11, the developing time being 6 minutes at 20 deg. The Hf line at 2940.77 I A was observable against the background, when the hafnium concentration was equal to a few thousandths of a percent.

Determination of unknown amounts of hafnium was carried out by means of a calibration curve drawn within the coordinates logarithm I^{Hf}/I^{Zr}, logarithm c, the background being taken into account. The line Zr 2942.3 A was used as the reference line. The spectra of standards were photographed on the same plates as those used for test samples. A typical calibration curve for the determination of HfO_2 in amounts ranging from a few thousandths to some tenths of a percent is shown in the diagram. The slope of the curve is about 0.67.

Appreciable amounts of CO and O_3 are formed in the discharge arc at 20 amperes. The work should therefore be carried out with adequate ventilation. The burning arc should be confined within a case with a door which can be conveniently opened.

Determination of Average Concentrations of Hafnium Oxide. Hafnium, at concentrations ranging from some tenths of a percent to a few percent, was determined on the average spectrographs Q-24 and ISP-22, using three-lens illumination of the slit. One drop of the test suspension in glycerol was placed by means of a pipet on the face of an unheated pointed carbon electrode. The metal stand and electrodes were placed on an electric hot plate, and the glycerol burnt off in the course of 20 minutes until no more fumes were given off. A thin layer of test material was, in this way, left on the electrode surface.

The spectrum was excited in a d.c. arc, the test material being connected to the anode.* The upper electrode was sharpened to give a truncated cone. The arc gap was 3.5 mm, the current was 6 amps., while exposure time was 30 seconds.

Analysis was carried out on the basis of a solid calibration curve using the analytical lines Hf 2641.4" — Zr 2619.2" A. The calibration curve was constructed within the coordinates logarithm I_{Hf}/I_{Zr}, logarithm c, the background being taken into account. The calibration curve is shown in the diagram. The slope was equal to one. The glycerol suspension should be used for analysis on the same day as it is prepared, since, on keeping the suspension for a long time, there occurs a gradual change in the relative intensities of the lines in the spectra.

DISCUSSION OF RESULTS

The techniques used most often for the determination of Hf in Zr are based on evaporation of test samples from the canal of a carbon electrode. In order to ensure more even burning of the test material, it is customary to mix the test sample with powdered graphite. Our earliest experiments on the determination of average amounts

* Analysis can also be carried out with an a.c. arc.

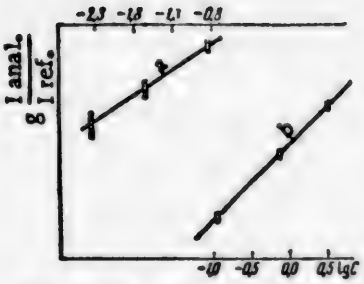

Diagram. Calibration curve for determination of Hf in Zr: a) For determination of low Hf concentrations; b) for determination of average amounts of Hf.

of hafnium by evaporation from a canal, showed that, even in the presence of graphite powder, sputtering of test material from the electrode canal was not a rare occurrence; this leads to weakening of the spectrum and to a sharp change in the relative intensities of the lines. This, in turn, leads to considerable experimental errors.

By placing the test material in the form of a suspension on a flat or almost flat electrode, sharp variations in the absolute intensity of the spectra can be avoided when the electrodes are set up properly and the interelectrode distances are reproduced readily. When this technique is used for introducing the test material into the discharge, even strong variations in the absolute intensity of the spectra do not affect the value of the relative intensities of the lines.

Experiments were carried out in order to clarify the effect of certain factors on the experimental accuracy. Spectra of samples containing approximately 1.3% and 0.8% of hafnium respectively, were photographed. The values of the blackening of the Hf lines were 0.8 – 0.9 and 0.45 – 0.5 respectively. The results are given in the Table. Changing the time for which the powder is triturated with glycerol from 5 to 35 minutes was found to have no effect on ΔS for the analytical pair of lines. A characteristic feature is that changes over wide limits in the amount of sample placed on the carbon had hardly any effect at all on the absolute intensity of the lines and on the values of ΔS. In order tc check this, emulsions containing 20, 40, and 60 mg of powder per ml of glycerol were prepared. The time for which the electrodes were dried on the electric hotplate after all the fumes had ceased to come off, was also found to have no effect.

The glycerol suspension gradually soaked into the carbon. A series of tests were therefore carried out to establish the effect of the soaking in of the glycerol into the carbon on the value of ΔS. No appreciable changes in the values of ΔS could be found between spectra obtained from electrodes dried immediately after placing the suspension on them, and spectra obtained from electrodes dried 2.5 hours after placing the suspension on them.

Effect of Various Factors on the Value of ΔS for the Lines Hf 2641.4 and Zr 2619.2 A

Duration of trituration of suspension			Amount of sample on the electrode			Time for which electrode was dried			Duration of soaking of the carbon with glycerol		
Time in min	ΔS	ΔS mean	Amount in mg	ΔS	ΔS mean	Time in min	ΔS	ΔS mean	Time in hours	ΔS	ΔS mean
7	0,04 0,06 0,08	0,06	20	0,29 0,26 0,28 0,25	0,27	6 *	0,22 0,19 0,20 0,22	0,21	Immediately after placing the glycerol on carbon electrode 2,5	0,26 0,25 0,29 0,29	0,27
14	0,07 0,05 0,06	0,06	40	0,27 0,31 0,27	0,28	20	0,24 0,27 0,25	0,25		0,29 0,28 0,30	0,29
21	0,06 0,08 0,06	0,07	60	0,26 0,25 0,28 0,26 0,29	0,27	50	0,26 0,27 0,25 0,24 0,24	0,25	—	0,31 —	—

* Incomplete burning off of the glycerol.

The fact that none of the factors listed above was found to affect the relative intensity of the lines, gives a favorable basis for carrying out analysis with satisfactory accuracy. This fact also permits analysis of samples containing average amounts of Hf by means of a constant calibration curve, without having to resort to photo-

graphing the spectra of standards. We had used glycerol suspensions previously for the determination of boron in boron carbide, and the technique fully justified itself in that case, also. This technique was borrowed from [8], which does not deal with the analysis of mixtures of Hf and Zr.

The reproducibility of the values of the relative intensities of the lines, in replicate photographs of the spectra of standards, and for samples of average concentration (0.2 – 3%) can be characterized by the following results. The maximum absolute deviation of the value of logarithm $I_{anal.}/I_{ref.}$ from their mean value (the spectrum of each sample was photographed 3 times) was equal to 0.03. In 83 cases out of a 100, this deviation was not more than 0.02; in 52 cases it was not more than 0.01. The maximum deviation of the value of logarithm $I_{anal.}/I_{ref.}$ is equal to 0.05. The probable error when three photographs of the spectra were taken was ± 2.1% for mean hafnium concentrations.

For samples with hafnium oxide concentrations equal to 0.005 – 0.007%, the experimental accuracy is lower. In this case the density of the Hf line differs insignificantly from the background and errors made during the photometric measurements start to play an essential role. The probable experimental error for thousandths of a percent of hafnium oxide, is ± 19% when three photographs are taken. The error drops to ± 13% when some hundredths of a percent is to be determined. For the determination of low concentrations, the spectra of three standards are taken on each photographic plate.

One worker can carry out ten analyses in the course of a working day.

SUMMARY

Methods have been developed for the quantitative spectrographic determination of 0.005 to 3% of hafnium in zirconium dioxide on the ISP-22 and KS-55 spectrographs. Samples are burnt as thin layers of powder on carbon electrodes. Experimental accuracy is sufficient for controlling the separation of hafnium from zirconium.

LITERATURE CITED

[1] L. N. Komissarova and V. E. Plinshchev, Prog. Chem. 25, 1197 (1956).

[2] D. M. Mortimore and A. Noble, Analyt. Chem. 25, 296 (1953).

[3] E. V. Gusiatskaia and A. K. Rusanov, J. Anal. Chem. 10, 75 (1955).*

[4] G. Kriuger, R. R. Shvangiradze and T. A. Mozgovaia, J. Anal. Chem. 10, 20 (1955).*

[5] G. W. J. Kingsbury and R. B. Temple, J. Appl. Chem. 1, 9, 406 (1951).

[6] V. A. Fassel and C. H. Anderson, J. Opt. Soc. America 40, 742 (1950).

[7] C. Feldman, Analyt. Chem. 21, 1211 (1949).

[8] R. C. Hughes, Analyt. Chem. 24, 1406 (1952).

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POTENTIOMETRIC TITRATION OF SILVER, COPPER, LEAD AND THALLIUM BY MEANS OF THIOACETAMIDE

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Thioacetamide CH_3CSNH_2 is used in analytical chemistry as a substitute for hydrogen sulfide for the precipitation of metals in qualitative and quantitative analysis. It is a solid which is fairly stable in neutral aqueous solutions, and, in contrast to hydrogen sulfide, does not possess toxic properties (it does not have an unpleasant odor). When thioacetamide is used as the precipitant, the metal sulfides are precipitated as coarse crystals which are readily filtered, and hardly trap foreign ions at all. By regulating the precipitation conditions, it is possible to alter the rate and sequence of the precipitation of the metal sulfides.

Thioacetamide was used by Ivanov in 1934 [1] for detecting heavy metals in pharmaceutical products. Vavilov [2] has recommended this reagent for the detection of bismuth. Subsequently, this reagent was used as a group reagent in qualitative analysis [3 – 5].*

The possibility of using thioacetamide for the gravimetric determination of heavy metals has been studied in detail by Flaschka and co-workers [6]. The same author has suggested using thioacetamide for the precipitation of metal sulfides in combination with complexons.

At present there is a very large number of examples of the use of thioacetamide for the determination of various metals [6 – 13].

We thought it would be interesting to study the possibility of using this reagent for the potentiometric titration of certain metals by precipitating them as their sulfides.

In the work described here an attempt was made to use thioacetamide as a titrant for the potentiometric titration of silver, copper, lead and thallium.

The main difficulty which arises during the use of thioacetamide as a source of hydrogen sulfide during potentiometric titration is its low rate of hydrolysis in aqueous solutions. According to the work carried out by Swift and Butler [13], the constant of the hydrolysis rate of thioacetamide at 90 deg has a value of 0.21 mole/liter. At higher pH values, and in the presence of lead ions, the constant of the hydrolysis rate increases by more than two orders. Under such conditions, the authors note that, in the presence of lead salts, the order of the reaction changes in comparison with hydrolysis in pure solutions.

The rate of precipitation of the metal sulfides is, in most cases, too low for the use of thioacetamide as a titrant during potentiometric titration.

Only precipitation of silver ions from ammoniacal solutions proceeds with sufficient speed for practical application. Other metal ions, such as copper, mercury, lead, thallium, etc. are precipitated very slowly by thioacetamide. Increasing the temperature and changing the pH of the solutions, although they affect the precipitation rate, in that they increase it, still do not do so to a sufficient extent to make the use of thioacetamide as a titrant for these metals feasible.

* Apparently, thioacetamide was used as a group reagent in qualitative analysis as long ago as 1928 (see [2]).

On the basis of a series of experiments which we carried out we found that the rate of precipitation of lead and some other metals by this reagent can be increased to a considerable degree by adding small amounts of hydrazine hydrate to the reaction mixture.

While in the case of precipitation of copper sulfide, the increase in the rate of precipitation in the presence of hydrazine hydrate can be ascribed to differences in the rate of precipitation of Cu^{+} as compared with that of Cu^{2+}, i.e. this increase can be explained by the reducing properties of hydrazine hydrate; in the case of the precipitation of the sulfides of lead, thallium, and other metals, such an explanation is no longer possible. The part played by hydrazine hydrate, in these cases, is, presumably, considerably more complicated, and requires special study.

Test element	Taken, in g	Found, in g	Difference in g	Test element	Taken, in g	Found, in g	Difference in g
Silver	0,1082	0,1085	+ 0,0003	Lead	0,1848	0,1850	+ 0,0002
	0,1134	0,1131	— 0,0003		0,1495	0,1493	— 0,0002
	0,1214	0,1209	— 0,0005		0,1583	0,1582	— 0,0001
	0,1358	0,1355	— 0,0003				
Copper	0,1026	0,1024	— 0,0002	Thallium	0,1968	0,1966	— 0,0002
	0,1148	0·1144	— 0,0004		0,1665	0,1668	+ 0,0003
	0,1206	0,1209	+ 0,0003		0,1327	0,1326	— 0,0001
	00,1336	0,1335	— 0,0001		0,0957	0,0954	— 0,0003
	0,1372	0,1373	+ 0,0001				

By making use of this property of hydrazine hydrate, we have developed techniques for the potentiometric determination of copper, lead and thallium by means of thioacetamide.

Titration was carried out with the aid of a sulfide indicator electrode made from synthetic argentite (Ag_2S); this electrode has been described previously [14]. The reference electrode was a saturated calomel electrode. The e.m.f. was measured on a PPTVI potentiometer. The compensation current was measured on a M91 galvanometer to 10 μa. The solution was agitated with a mechanical stirrer during titration. The thioacetamide solution was prepared by dissolving material which had been recrystallized twice (m.p. 110 deg) from benzene in distilled water. The thioacetamide solution was standardized against an accurately weighed aliquot of a sample of the test metal.

The thioacetamide solution was stored in a flask with a ground-glass stopper. The factor of the thioacetamide solution remained constant over a long period (about 2 months), and the solution did not require any special storage conditions.

Determination of Silver. From ammoniacal solutions, in the presence of sodium or calcium ions, precipitation of silver ions by thioacetamide proceeds instantaneously. The electrode potential is established very rapidly during titration, and titration proceeds without any complications. A typical titration curve obtained during titration of silver with thioacetamide is shown in Fig. 1.

As the results given in Table 1 show, the accuracy obtained during determination of silver by titration with thioacetamide is not less than the accuracy of methods widely used in practice.

Preparation of samples for analysis, and the titration itself are carried out as follows: 0.1 — 0.2 g of silver is dissolved in the minimum amount of nitric acid, the solution is then evaporated almost to dryness for removal of nitrogen oxides. The crystals obtained are dissolved in a small amount of water and the solution transferred to a 100 ml standard flask. 10 ml of this solution, which is taken for titration, is placed in the titration cell and 20 ml of the following mixture added: 0.2 N NH_4OH + 0.2 N $NaNO_3$ + 0.03 N $Ca(NO_3)_2$.

Titration is carried out in the cold with stirring. Calculations are based on the factor of the thioacetamide which has been established by means of a standard sample of silver under the same conditions. The equivalence point is established by constructing a curve within the coordinates $d\epsilon/dv$, V.

Determination of Copper. Precipitation of copper sulfide by means of thioacetamide from solutions containing divalent copper, proceeds only after long standing — even on heating. Appreciably more rapid is the precipitation of copper sulfide from solutions of univalent copper obtained by reducing the divalent copper with hydrazine hydrate.

In such cases cuprous sulfide is formed immediately, even at room temperature. The potential of the sulfide electrode is established very rapidly during titration. A curve obtained during titration of copper with thioacetamide is shown in Fig. 1. As in the case of silver, the titration curve exhibits a large potential jump near the equivalence point.

Preparation of samples for analysis is carried out in exactly the same way as for silver. For one determination 10 ml of a solution of divalent copper with a content of 0.01 — 0.015 g of Cu is taken, and 30 ml of 1 N sodium acetate and 5 ml of NH_4OH (25%) added, hydrazine hydrate (1:5) is then added until the blue color disappears.

Thioacetamide is added with stirring to the mixture thus obtained. Reduction of the copper must be carried out very carefully, precautions being taken to ensure that the amount of hydrazine hydrate taken is such that a large excess of it does not remain in the solution. When a large excess of this material is present, the electrode potential is established poorly and titration is not quantitative. The reproducibility and accuracy of the results obtained for the determination of copper are fully satisfactory (Table 1). Calculations are based on the factor for thioacetamide established beforehand by means of a standard copper sample.

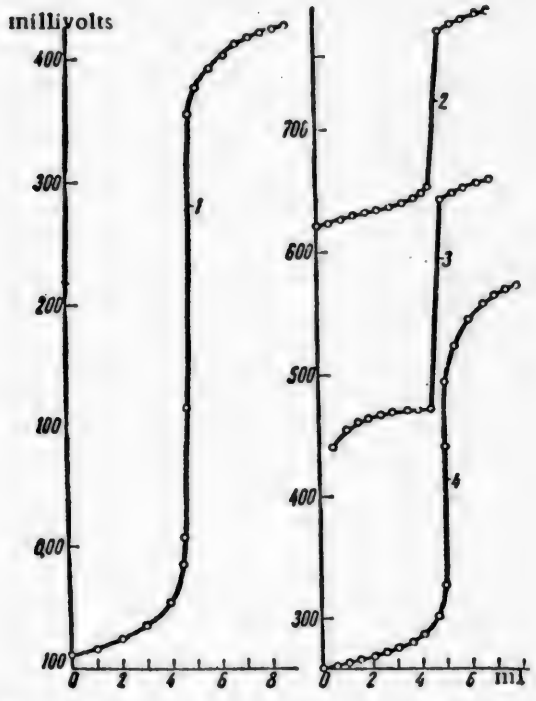

Fig. 1. Titration curves of metals with thioacetamide:
1) Silver; 2) lead; 3) thallium; 4) copper.

Fig. 2. Titration curves for a mixture of silver and copper ions.

Determination of lead is carried out in the same way as for silver and copper. To 10 ml of a solution containing 0.01 — 0.015 g of Pb is added 10 ml of 10% NaOH and the solution heated to 70 — 80 deg, a few drops of hydrazine hydrate is then added. A curve obtained during titration of lead with thioacetamide is shown in Fig. 1.

As is evident from Table 1, the results obtained for lead proved to be very good.

Determination of Thallium. Flaschka [11] has shown that univalent thallium is not precipitated from neutral and acetic acid solutions by means of thioacetamide; from ammoniacal solutions, thallium sulfide precipitates instantaneously. Nevertheless, the potential of the sulfide electrode is established poorly in ammoniacal solutions. Addition of small amounts of hydrazine hydrate renders the potential of the sulfide electrode more stable. The stability of the potential is also enhanced by heating the solution.

The curve obtained during titration of thallium with thioacetamide has a characteristic shape (Fig. 1). The potential jump at the equivalence point is very sharp; nevertheless, its absolute value is less than that of the other metals studied. The sharp jump on the titration curve can be observed at concentrations down to 2 – 3 γ of Tl in 10 ml of solution.

Metal thallium is dissolved in dilute nitric acid. 10 ml of solution containing 0.01 – 0.02 g of Tl is taken for titration, 25 ml of water is added and the solution warmed 70 – 80 deg; 25 ml of 25% NH_4OH is then added, followed by 2 – 3 drops of hydrazine hydrate (1:2).

The thioacetamide solution was standardized against a standard solution of thallium nitrate. As Table 1 shows, the results obtained for the potentiometric determination of thallium are accurate enough.

For the determination of silver and copper in copper-silver alloys, using one aliquot of test sample, use was made of, on the one hand, differences in the solubility of the sulfides of copper and silver, and, on the other hand, of differences in the precipitation rate of these sulfides.

As mentioned already, direct precipitation of divalent copper by thioacetamide proceeds extremely slowly from ammoniacal solutions, while silver sulfide is precipitated immediately from such solutions. Accordingly, we titrated silver and copper in such a way that silver was precipitated first from ammoniacal solution, while the copper was then reduced with hydrazine hydrate and finally precipitated with thioacetamide.

In Fig. 2 are shown the curves obtained during titration of mixtures of silver and copper. The titration curves show two potential jumps corresponding to successive precipitation of silver and copper. The most accurate results were obtained for copper contents ranging from 10 to 90%.

The alloys were prepared for analysis in the same way as the separate metals. To 10 ml of solution containing from 0.01 to 0.05 g of silver, and itself contained in the titration cell, is added 30 ml of a mixture of 0.2 N $NaNO_3$ and 0.03 N NH_4OH; titration is carried out until the first potential jump, corresponding to completion of precipitation of silver, is reached; to this solution is then added 5 ml of 25% ammonia solution, followed by several drops of hydrazine hydrate (1:5), and the titration continued until the second potential jump is reached; this corresponds to completion of precipitation of copper.

Calculations are based on factors for the thioacetamide established beforehand for each metal separately.

The accuracy for the determination of silver is the same as that obtained during determination of silver in pure solutions of silver. The results obtained for copper are on the high side.

SUMMARY

1. It has been shown that it is possible to use thioacetamide for potentiometric titration of metals precipitated as sulfides.

2. Conditions have been established for the potentiometric titration of silver, copper, lead, and thallium, and also for silver-copper alloys in which thioacetamide is used as the titrant.

LITERATURE CITED

[1] F. V. Ivanov, Soviet Pharmacy, No. 5, 16 (1934).

[2] N. V. Vavilov, J. Appl. Chem. 11, 356 (1936).

[3] H. Barbar and E. Greskowiak, Ind. End. Chem., Anal. Ed. 21, 192 (1949).

[4] T. Lipiec and H. Pryszewska, Przem. chem. 7, 349 (1951).

[5] H. Barbar and T. Taylor, Semimicro Qualitative Analysis. Harper and Bros. N. Y., (1933).

[6] H. Flaschka, Chemist-Analyst, 44, No. 1, 2 (1955).

[7] H. Flaschka and H. Lykobljiwich, Analyt. chim. acta 4, 247, 351, 356, 482, 486, 602, 606 (1950); 5, 60, 152 (1951).

[8] H. Flaschka and H. Abdine, Chemist-Analyst 44, 8 (1955).

[9] H. Flaschka, Z. analyt. Chem. 133, 103 (1951).

[10] F. Pohe, Angew. Chemie. 66, 603 (1954).

[11] H. Flaschka, Z. analyt. Chem. 137, 107 (1952).

[12] I. Valentin and D. Stehwien, Fürtig W. Farmazja 8, 638 – 642 (1953).

[13] H. Swift and A. Bytler, Analyt. Chem. 28, No. 2, 146 – 153 (1956).

[14] V. A. Kremer and E. I. Vail', Zav. Lab. 23, 146 (1957).

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A SIMPLIFIED METHOD FOR INTERNAL ELECTROLYSIS USING A DIAPHRAGM

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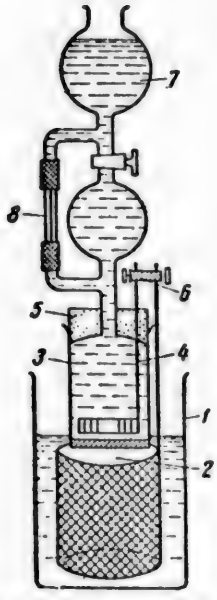
Of the existing methods used in analytical chemistry for internal electrolysis, only those which do not involve diaphragms have received wide practical application [1]. Diaphragm methods of internal electrolysis [2] are used much more rarely in view of the complexity of the apparatus and the duration of the electrolysis process which is determined by the high ohmic resistance of the electrolyzer. The method of internal electrolysis with a protective film [3], although it is simple from the point of view of the design of the apparatus, is nevertheless still inferior to the diaphragmless method from the point of view of the duration of electrolysis, and, at the same time, in contrast to the diaphragm method, it is not applicable for the determination of large amounts of metal.

Were it possible to eliminate the phenomenon of cementation by a simpler method, then, undoubtedly, the internal electrolysis method, in view of its simplicity and convenience, would receive even more wide application in analytical practice.



Schematic diagram of the apparatus used for internal electrolysis using a No. 1 coarse-pore diaphragm.

Bearing in mind the advantages of internal over external electrolysis, we decided to study the possibility of developing a simplified diaphragm method which would permit separation of average and large amounts of metal, fairly rapidly.

In order to speed up the process of metal deposition, we departed from the use of thick diaphragms, and used No. 1 large-pore glass diaphragms, the introduction of which into the electrolyzer does not increase the ohmic resistance of the latter significantly. Penetration of catholyte into the anode space was prevented in the method under test by meeting the catholyte liquid with a weak flow of anolyte; this, needless to say, is necessary only in the initial period of electrolysis, in the course of the 10 – 15 minutes when most of the test material is deposited from solution. After this, possible mixing of the solutions should not present any danger, since, at low concentrations of test material, cementation will not occur.

The apparatus suggested by us for internal electrolysis is shown schematically in Fig. 1. The apparatus consists of a beaker 1, with a capacity of 250 – 300 ml, into which the test solution is poured, a platinum grid cathode 2, a glass beaker 3, 80 mm tall and 40 mm in diameter, with a bottom made from No. 1 coarse-pore glass, and designed for separating the anode space from the cathode space. A beaker of this type is readily made from a normal glass funnel with a No. 1 porous filter disc, by cutting off the conical part of the funnel below the disc, and rounding off the edges after cutting off level with the base of the disc. The top of the beaker is closely sealed with a rubber stopper 5 with two holes drilled through it; through one of these holes is fitted a tube from the supply reservoir containing the anolyte, while through the other hole is fitted the upper part of the anode 4 for connecting it through a brass terminal to the

cathode. Connection of the anode with the cathode is made in such a way that the top part of the cathode grid is at the same level as the porous bottom of the beaker 3. The supply reservoir is a dropping funnel of a modified type with a spherical bulb underneath the tap, and two side tubes between which a capillary 7 is fitted by means of rubber tubing. Through this capillary, when the tap of the reservoir is closed, the anolyte passes slowly into the beaker 3, thereby creating the necessary head of anolyte liquid on the diaphragm; thanks to this, penetration of catholyte into the anode space is completely prevented.

The experimental procedure used was as follows. The supply (pressure) reservoir and the diaphragmed beaker containing the anode were filled with anode liquid. This was carried out by opening the tap of the reservoir, and placing a tall beaker containing anolyte heated to 70 – 80 deg under the diaphragmed beaker; the anolyte was then sucked by mouth or by means of a water pump through the upper part of the reservoir. After connecting the anode to it, the apparatus was immersed in the test solution of cupric sulfate heated beforehand to 70 – 80 deg, so that only the lower part of the diaphragmed beaker was in the solution. Completeness of deposition of copper was controlled by a spot test with potassium ferrocyanide or sodium sulfide. The time taken for complete deposition of copper, depending on the amount of copper, varied from 40 to 90 minutes. When electrolysis was complete, the apparatus was rapidly removed from the solution and immersed in distilled water for several minutes; the cathode was then disconnected, washed with water and then with alcohol, dried, and, after cooling, weighed.

TABLE 1

Determination of Copper by the Simplified Method of Internal Electrolysis (anolyte – potassium chloride)

Copper taken, in mg	Copper found, mean of 3 – 4 determinations, in mg	Duration of electrolysis, in minutes	Mean deviation of individual determinations from the mean		Deviation of the mean value found from that taken	
			in mg	in %	in mg	in %
46.85*	46.73	40	0.30	0.63	0.12	0.25
118.8 *	118.5	55	0.50	0.43	0.30	0.26
142.8 *	142.5	65	0.00	0.00	0.30	0.21
190.8 *	190.5	80	0.20	0.10	0.30	0.14
238.5 *	238.4	90	0.20	0.08	0.10	0.05
142.8 **	141.7	65	0.20	2.10	1.10	0.80
253.0 ***	252.8	90	0.10	0.06	0.20	0.07

* Zinc anode
** Iron anode
*** Aluminum anode

Pure reagents were used in the course of the experiments carried out. The zinc and aluminum anodes were prepared from the chemically pure metals. The solution of cupric sulfate was standardized by external electrolysis. The solution was prepared for analysis in the usual way. Solutions of potassium chloride and potassium nitrate were used as the anolyte.

Tests showed that the suggested method of internal electrolysis permits determination of both average and large amounts of copper.

It should be pointed out that when a zinc, or an iron anode immersed in a saturated solution of potassium chloride was used, dissolution of the anode proceeded slowly and was not accompanied by evolution of appreciable amounts of gas. When, however, an aluminum anode was used, the anode dissolved vigorously and considerable amounts of hydrogen were evolved. In order to prevent expulsion of anolyte from the diaphragmed beaker,

and to prevent the cessation of current flow which accompanies this, the apparatus was provided with the spherical vessel under the tap in order to collect the gas.

As is evident from Table 1, the accuracy and reproducibility of the results for copper are fully satisfactory.

Results for the determination of copper with a zinc anode immersed in a saturated solution of potassium chloride, in solutions containing some ferrous sulfate in addition to copper, are given in Table 2. As can be seen from Table 2, the presence in the test solution of iron, even in amounts which are twice that of copper, does not affect the results for copper

TABLE 2

Determination of Copper in the Presence of Divalent Iron

Copper taken, in mg	Iron added, in mg	Copper found, in mg	Mean deviation of the individual determinations from the mean		Deviation of the mean found from that taken	
			In mg	In %	In mg	In %
238,2	224,0	237,6	0,30	0,40	0,60	0,24
238,2	448,0	237,4	0,20	0,20	0,80	0,33

Special tests showed that other salts of the alkali metals can be used instead of potassium chloride as the anolyte.

In conclusion, the applicability of the method we had developed was checked for the determination of copper in alloys. A standard sample of Muntz metal certified as containing 60.40% of copper was taken for analysis. The alloy was dissolved, and the solution obtained prepared for analysis in the usual way. The determination was carried out with the aid of a zinc anode. The mean value for five determinations was 60.39%.

SUMMARY

A simplified apparatus has been designed for internal electrolysis in which a diaphragm made of a No. 1 large-pore glass plate is used. It has been shown that it is possible to determine average and large amounts of copper by means of this apparatus with reasonable accuracy and rapidity.

LITERATURE CITED

[1] Iu. Iu. Lur'e, Trans. All-Union Conference on Anal. Chem. Vol. 1, pg. 231 (1939).

[2] Iu. A. Chernikhov and E. V. Shtutser, Zav. Lab. 8, 801 (1939).

[3] Iu. A. Chernikhov and G. A. Bol'shakova, Zav Lab. 14, 3 (1948).

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THE DETERMINATION OF MICRO AMOUNTS OF COPPER, LEAD, AND ZINC IN NATURAL WATERS AND IN SOIL EXTRACTS

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The coexistence of copper, lead, and zinc is common for natural waters in territories where polymetallic ore deposits are found. An interest in a simple field method of determining the elements is therefore a natural one.

The separation and determination of copper, lead, and zinc by means of dithizone is based on accurate control of the pH of the solutions and the use of cyanide for masking Cu and Zn during determination of lead [1, 2]. The poisonous nature of KCN is the most essential drawback for its use in the field. Moreover, potassium cyanide can lead to low results for lead [1, 3].

Two methods have been developed for the separation and subsequent determination of Cu, Pb, and Zn, in which potassium cyanide is not used.

In the first variant, copper is removed by extraction of the dithizonate in a hydrochloric acid medium (0.1 – 0.5 N), or the total dithizonates of copper, zinc, and lead are extracted in a weakly ammoniacal medium in the presence of ammonium citrate and the lead and zinc then re-extracted with 0.01 – 0.02 N HCl.* In both cases copper is determined on the basis of the mixed color in the organic extract. The aqueous layer is made alkaline with ammonia and the dithizonates of zinc and lead extracted. We have found that at sufficiently low pH values (about 6), an aqueous solution of thiosulfate will readily re-extract lead from the extract without touching the zinc dithizonate. When the separated aqueous re-extract is subsequently made alkaline with ammonia, the lead is again extracted with a solution of dithizone in CCl_4 and the lead is then determined by the monochromatic method [1]. The zinc remaining in the organic layer is evaluated by comparison with standards, or is re-extracted and titrated with dithizone.

The second method is based on differences in the stability of the diethyldithiocarbamates of copper, lead, and zinc dissolved in carbon tetrachloride, with respect to hydrochloric acid. In aqueous acid solutions, diethyldithiocarbamic acid breaks down rapidly [4]. On the other hand, heavy metal carbamates extracted by carbon tetrachloride are much more difficult to break down with acids [5, 6]. A study of the stability of the carbamates of copper, lead, and zinc dissolved in CCl_4 led us to conclude that it should be possible to separate these metals by re-extraction with hydrochloric acid of varying concentrations. Zinc carbamate is completely re-extracted with 0.1 N HCl, which does not, however, affect lead carbamate. Lead carbamate is decomposed by 1.0 N HCl (completely by 3 N HCl). Copper carbamate is not decomposed even on shaking with 6 N HCl. Zinc and lead are determined in the re-extracts by means of dithizone.

a) Separation of Zinc and Lead by Means of Thiosulfate. The analytical procedure followed depends on whether water or an acid extract of solid materials is being analyzed. During the analysis of large volumes of test water, preliminary acidification, which is necessary for the extraction separation of copper, is undesirable,

* Extraction is best carried out in an acid medium when low volumes of test solution are dealt with, while when large volumes (because of the necessity of preparing large amounts of very pure HCl and ammonia) of test solution are being examined extraction is best carried out from a weakly ammoniacal medium.

because of the possibility of introducing contamination with the HCl. To 0.5 liter of the test water was added 2 ml of a 25% solution of ascorbic acid or 5 ml of a saturated solution of ammonium citrate purified by means of dithizone, and the pH of the solution adjusted to a pH of 8 – 8.5 with ammonia. Using 5 ml lots of a solution of dithizone in CCl_4 for extracting, the mixture of dithizonates of copper, zinc, and lead was extracted from the solution by vigorous shaking for 3 minutes. Extraction was repeated with fresh lots of dithizone until the dithizone ceased to change color. The combined extracts were then shaken for 2 minutes with two lots of 5 ml of 0.10 – 0.15 N HCl and these re-extracts combined. The CCl_4 layer was washed with 10 ml of "the metal-free" water, which was also combined with the re-extract. The re-extract contained the zinc and lead, while copper remained in the organic layer. Copper dithizonate was broken down by evaporating the CCl_4 and lightly calcining the residue; copper was then determined in hydrochloric acid solution as its dithizonate by the mixed or monochromatic methods [1]. The re-extract containing Zn and Pb was neutralized to phenol red by means of ammonia, and was then titrated with dithizone to a small excess of the latter. The extract was washed with ammonia (1:300) in order to remove excess dithizone, and then washed with the "metal-free" water, after which it was shaken up with 5 ml of 10% $Na_2S_2O_3 \cdot 5H_2O$ solution for 1 minute, the thiosulfate solution had been purified beforehand with dithizone and its pH adjusted to 5.5 – 6.0. The pH of the thiosulfate solution was regulated (on the day the analysis was carried out) by means of 0.01 N HCl, the latter being added dropwise with stirring. Measurements were made with a glass electrode; nevertheless, it was found that it was sufficient, when dealing with the same batch of reagent, simply to prepare a small amount of solution and establish the number of drops of 0.01 N HCl that need to be added to 50 ml of the solution (usually 1 – 3 drops); in this way there is no need to resort to a pH meter but simply use the number of drops of HCl already established. The re-extract was made alkaline with ammonia to the phenol-red endpoint; lead was then determined by extraction titration with a solution of dithizone in CCl_4, the dithizone factor with respect to lead being 2 – 4 γ.

TABLE 1

Determination of Zinc and Lead

pH of thiosulfate solution	Amount of lead found in the aqueous layer as a percentage of that taken	Zn found in the CCl_4 layer after re-extraction of Pb, as a percentage of the Zn taken
6.5	50	125–100
6.2	60–80	110–100
6.0	80–100	~ 100
5.8	80–100	~ 100
5.6	80–100	~ 100
5.4*	90–110	~ 100
5.3**	> 100	~ 100

* At low ratios of Pb:Zn the results were high for Pb.

** The results for Pb were often high. Rapid decomposition of thiosulfate.

After removal of the lead, zinc was determined directly in the CCl_4 layer (when the color corresponded to that of one of a standard series) or by re-extraction with 0.01 – 0.02 N HCl; in the latter event, after re-extraction, the solution was neutralized with ammonia to the phenol-red endpoint, and the zinc was determined like lead, by extraction titration, the dithizone factor with respect to zinc being 1 – 2 γ Zn.

During the analysis of hydrochloric extracts it was found best to choose the volume of aliquot to be taken on the basis of the "total metals"* content determined beforehand. "Total metals" was determined on a separate

* An empirical value determined during hydrochemical exploration by titrating a sample of water in a weakly alkaline medium with dithizone. In samples of water taken in territories where polymetallic ore deposits are found, this value generally reflects the zinc content.

aliquot, the solution was neutralized with ammonia to a pH of 8 – 8.5 in the presence of ascorbic acid and the solution then titrated with dithizone as for zinc determination. For the separate determination of Cu, Zn, and Pb, an aliquot was then taken containing 10 – 25 γ of "total metals". The chosen solution was neutralized with ammonia to an approximately neutral or weakly acid reaction, when it was diluted with an approximately equal volume of 0.10 – 0.20 N HCl, and 2 ml of a 25% ascorbic acid solution added. In the acid extracts one often came across appreciable amounts of iron, for complexing which, large amounts of citrate were required, and even this did not always prevent oxidation of the dithizone. Moreover, we found that copper, in the presence of citrate, is very slowly extracted from acid solution by dithizone. It was found that ascorbic acid while reducing Fe^{3+} to Fe^{2+} did not interfere at all with the extraction of copper, and prevented dithizone from being accidentally oxidized during titration. Copper was titrated with dithizone, the latter being standardized against zinc in an alkaline medium, and against copper in an acid medium. After the determination and simultaneous separation of copper, the aqueous solution containing Zn and Pb was adjusted to a pH of 8 to 8.5 with ammonia (established by withdrawing an aliquot for test or from the change in color of iron ascorbate present in the solution), and the zinc and lead were then determined as described above.

It is obvious from Table 1 that the optimum pH limits for the re-extraction of lead by thiosulfate are 5.5 – 6.0.* At higher pH values, lead is not extracted completely, while at lower values zinc is also re-extracted to some extent with the lead.

b) Separation of the Carbamates of Copper, Lead, and Zinc by Re-extraction with Hydrochloric Acid. To the test sample of water was added 10 ml of 5 N $CaCl_2$ purified with dithizone, 2 ml of 5% sodium diethyldithiocarbamate solution, and 10 ml/liter of a saturated solution of ammonium citrate, and the pH of the solution adjusted to 8.5 – 9 (phenol red or thymol blue). 15 ml of carbon tetrachloride was then added and the whole shaken vigorously for 5 minutes. The volume of test water was 0.5 liter or less.** After standing, the CCl_4 layer was transferred to a small separating funnel. Colorimetric measurements were carried out on the colored copper complex immediately, or after re-extraction of zinc and lead. Zinc was re-extracted by shaking four times with 5 ml lots of 0.1 N HCl for 1 minute periods. In the combined re-extracts (or an aliquot part) zinc was determined as in a) by extraction titration with dithizone.*** The carbon tetrachloride which then only contained copper and lead carbamates was washed with "metal-free" water for removal of residual copper and lead carbamates; lead was then re-extracted from it by shaking it twice, for 1 minute each time with 5 ml lots of 3 N HCl. It is extremely important to use acid free from traces of metals. Normally zinc is present in the commercial acid (even the best grade) and this increases the results for lead sharply. Naturally, both during the zinc determination (after re-extraction with 0.1 N HCl), and, particularly, during the lead determination, it is essential to introduce corrections by carrying out a blank. Acid of the requisite normality (particularly for re-extraction of lead) is best prepared from acid distilled by the "cold method" [7]. Ammonia solution can be prepared from the commercial solution by adding solid alkali to the latter, and then passing the gaseous ammonia liberated through twice-distilled water cooled with ice.

The re-extract containing the lead is neutralized with ammonia to the phenol-red endpoint and the lead then determined as indicated in a).

It is clear from Table 2 that there is a good separation of copper, zinc, and lead. Only in the case of very low amounts of lead (2 – 4 γ) is there observed appreciable increases (up to 100%) in the results for lead as a result of inclusion of traces of zinc. When, however, potassium cyanide is used, low results are obtained as shown by results which we obtained and by published results [1, 3].

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* A purified solution of thiosulfate will keep its pH unchanged for a long time as long as it is not acidified. Accordingly, having established the amount of acid (usually 1 – 3 drops of 0.01 N HCl per 50 ml of $Na_2S_2O_3$) necessary, there is no need to use the pH-meter further.

** The amounts of the acid extracts (which normally contained large amounts of micro elements) taken were such that they contained 10 – 100 γ ΣM, and the amount of $CaCl_2$ was reduced proportionally. The diethyldithiocarbamate solution was added after neutralization of the acid and complexing of the iron.

*** For an initial volume of test water of 0.5 – 1 liter, the results for zinc is multiplied by 1.2. For volumes up to 100 ml there is no need for a correction.

TABLE 2

Determination of Cu, Zn, and Pb After Re-extraction of Zn and Pb Carbamates From a Layer of CCl_4

Cu γ/l		Zn γ/l		Pb γ/l		Cu γ/l		Zn γ/l		Pb γ/l	
taken	found	taken	found	taken	found	taken	found	taken	found	taken	found
5	5	5	5	5	6	20	20	30	28	10	11
10	9	10	10	10	9	10	10	20	19	2	4
20	20	20	22	20	18	—	—	50	48	4	7
30	30	45	40	5	4	10	10	50	49	4	5
40	40	40	36	40	40	50	50	50	48	4	4
2	2	2	2	2	2						

* The extraction of the total carbamates of metals was carried out in the first six experiments from one liter of solution, and in the remaining experiments, from 1.5 liters. The re-extraction of zinc was done with 0.1 N HCl and re-extraction of Pb was done with 3 N HCl.

SUMMARY

A method has been developed for the quantitative separation of lead from a mixture of the dithizonates of zinc and lead (after separating copper in the usual way) by treatment with thiosulfate at a pH of 5.5 – 6.0. The re-extracted lead is determined by titration with dithizone at a pH of about 8.5.

A method has been developed for the separate determination of copper, zinc and lead diethyldithiocarbamates by treatment with HCl solutions of different concentrations, and subsequent titration with dithizone.

The two methods do not require the use of potassium cyanide and are suitable for field geochemical work.

LITERATURE CITED

[1] E. B. Sandell "Colorimetric Determination of Traces of Metals", [Translated from English], Goskhimizdat, Moscow (1949).

[2] E. B. Sandell, Industr. and Engng. Chem., Anal. Ed. 9, 464 (1937).

[3] H. B. Elkins, Chem. Abst. 47, 10402f (1953).

[4] H. Bode, Z. analyt. Chem. 142, 414 (1954).

[5] Iu. A. Chernikhov and B. M. Dobkina, Factory Lab. 15, 1143 (1949).

[6] Iu. A. Chernikhov and B. M. Dobkina, Factory Lab. 15, 906 (1949).

[7] Iu. V. Kariakin and I. P. Angelov, "Pure Chemical Reagents, Method 2", [in Russian], GONTI, p. 283 (1955).

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SEPARATION OF TITANIUM FROM ACCOMPANYING ELEMENTS BY ION EXCHANGE CHROMATOGRAPHY

COMMUNICATION 3. SEPARATION OF TITANIUM AND ZIRCONIUM*

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In order to establish the possibility of carrying out a chromatographic separation of quadrivalent titanium and zirconium, a study was made of their sorption by ion exchange resins from hydrochloric acid solutions. The use of hydrochloric acid solutions in chromatography is interesting from the point of view of anion and cation exchange, since, very often, a small change in the acid concentration can lead to a significant difference in the sorptive capacity, even of elements with very similar properties [1 – 8].

The sorptive capacity of the elements has been studied by many different methods (by analysis of the solution flowing out of the column, by determining the distribution of an element on the column,etc.). A method which is convenient and simple enough, in our opinion, is the method of determining partition coefficients, this consists of shaking an accurately known amount of the air-dry resin until equilibrium is reached with a known volume of test solution, an aliquot of the solution is then taken and the amount of the element which has not been adsorbed on the resin determined. The distribution coefficient φ is calculated by means of the formula [9]:

$$\varphi = \frac{M_1}{M - M_1} \frac{V}{m}$$

where M_1 is fraction of the element in the resin in milligrams; M is the total amount of the element contained in the original solution, in milligrams; V is the volume of solution; and m is the weight of the resin.

As in previous work, we determined the comparative sorption of these elements by this method. In our experiments V and m were kept constant at 60 ml and 0.5 g,respectively. The concentration of the quadrivalent titanium solution was 1.49×10^{-4} mole/liter, while that of the zirconium was 8.97×10^{-5} mole/liter. The ion exchange resins tested were the cation exchange resins SBS, KU-2 and the anion exchange resins EDE-10 and AN-2F. The resins were washed free from impurities before use; SBS and KU-2 were converted into the H-form while EDE-10 and AN-2F were converted into the Cl-form. The titanium concentration of the equilibrium solutions was determined photometrically by means of chromotropic acid, while the zirconium concentration was determined by means of arsenazo.**

It was established that neither titanium nor zirconium is sorbed by the anion exchange resins from 0.1 – 6 N solutions of hydrochloric acid. The results obtained with the cation exchange resins are given in Table 1.

It follows from Table 1 that, in comparatively dilute hydrochloric acid solutions (0.1 – 1 N), zirconium is completely sorbed by both cation exchange resins. This indicates that, under the given conditions, zirconium exists in solution as positively charged ions. At higher acid concentrations there is observed some difference in the sorption of the element by the cation exchange resins: SBS, though only to a negligible extent, still does

* Communication 2, See J. Anal. Chem. 12, 377 (1957).

** Benzene-2-arsonic-acid <1-azo-2> 1,8-dihydroxynaphthalene-3,6-disulfonic acid.

TABLE 1

Partition Coefficients for Quadrivalent Titanium and Zirconium in Hydrochloric Acid Solutions on SBS and KU-2

Normality of HCl solution	SBS		KU-2	
	D_{Ti}	D_{Zr}	D_{Ti}	D_{Zr}
0,1	216,0	Completely absorbed	713,8	Completely absorbed
1	10,3	"	Not absorbed	"
2	Not absorbed	116,0	"	56,3
4	"	17,4	"	Not absorbed
6	"	11,2	"	"

TABLE 2

Chromatographic Separation of Titanium and Zirconium on KU-2 by Means of Hydrochloric Acid

Ratio Ti : Zr	Ti taken, in mg	Volume of 1 N HCl, in ml	Ti found, in mg	Zr taken, in mg	Volume of 4 N HCl, in ml	Zr found, in mg
1000 : 1	200,0	400	201,0	0,200	50	0,198
1000 : 1	200,0	400	200,0	0,200	50	0,196
1 : 1	1,000	150	0,999	0,997	100	0,990
1 : 1	1,000	150	1,000	0,997	100	0,992
1 : 1	1,000	150	0,990	0,997	100	0,986
1 : 100	0,050	150	0,050	5,000	175	4,942
1 : 100	0,050	150	0,050	5,000	175	4,983
1 : 10000	0,005	75	0,005	50,16	200	50,14
—	0,005	75	0,005	50,16	200	50,13

sorb Zr from comparatively acid solutions. Sorption of titanium in the HCl concentration range 0.1 – 1 N is low and does not occur in more acid solutions. This, presumably, cannot be explained by formation of anionic complexes, since no sorption of this element by the anion exchange resins was observed.

Differences in the sorption of titanium and zirconium in 1 N HCl gave us a basis for developing the following method for separating these elements. A column (11 cm long and 0.5 cm in diameter) was filled with KU-2 resin in the H-form and the resin washed with 1 N HCl; the test solution containing titanium and zirconium chlorides, and 1 N with respect to HCl, was then introduced into the column. The column was washed with 1 N HCl until all the titanium had been extracted; the zirconium was eluted with 4 N HCl. Results of such separations are given in Table 2.

The results of these separations can be regarded as satisfactory. Reactions for zirconium in the titanium solutions, and for titanium in the zirconium solutions gave negative results. SBS cannot be recommended for separating these elements, since, in the first instance, for elution of equal amounts of titanium, approximately 2.5 times more 1 N HCl is required, while, secondly, 4 N HCl elutes only 80 – 85% of the zirconium from this resin.

SUMMARY

1. The partition coefficients of quadrivalent titanium and zirconium between the ion exchange resins SBS and KU-2, and hydrochloric acid solutions of various concentrations have been determined. It has been established that these elements are not sorbed from 0.1 – 6 N hydrochloric acid solutions by the anion exchange

resins EDE-10 and AN-2F.

2. A method has been developed for the quantitative chromatographic separation of titanium and zirconium at ratios of Ti:Zr from 1000:1 to 1:10,000 by means of a hydrochloric acid solution on the cation exchange resin KU-2.

LITERATURE CITED

[1] K. A. Kraus and F. Nelson, Collection "Chemistry of Nuclear Fuels", Goskhimizdat, Moscow – Leningrad, p. 353 (1956).

[2] I. Sasaki, Bull. Chem. Japan 28, 89 (1955).

[3] E. H. Huffman and R. C. Lilly, J. Amer. Chem. Soc. 71, 4147 (1949); 73, 4474 (1951).

[4] E. C. Campbell and F. Nelson, Phys. Rev. 91, 499A (1953).

[5] E. Blasius and M. Negwer, Naturwissenschaften 39, 257 (1952).

[6] E. Blasius and U. Wächtel, Angew. Chem. 66, 305 (1954).

[7] N. K. Shchipakina, E. M. Nemirovskaia, and M. M. Seniavin, J. Anal. Chem. 12, 7 (1957).*

[8] D. Jentzsch and I. Frotscher, Z. analyt. Chem. 144, 1 (1955).

[9] E. R. Tompkins and S. W. Mayer, J. Amer. Chem. Soc. 69, 2859 (1947).

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DETERMINATION OF DI- AND TRIVALENT TITANIUM IN CHLORIDE MELTS BY MEANS OF FERRIC CHLORIDE

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Detailed study of the electrolysis of salt melts containing titanium necessitates the separate determination of di- and trivalent titanium in the electrolyte. Existing methods for the determination of titanium in low valency states [1, 2] do not always give satisfactory results. In several instances it is of interest to determine the valency states of titanium directly in the salt melt, without cooling it and getting the titanium into solution.

The most suitable approach seemed to be oxidation of di- and trivalent titanium directly in the salt melt by ferric chloride, with parallel determination of trivalent titanium in an aqueous solution of the electrolyte. This approach would permit separate determination of the amount of Ti^{II} and Ti^{III} in each others presence. Nevertheless, this method also is complicated by the thermal dissociation of ferric chloride, and by its volatility [3].

At high temperatures $FeCl_3$ decomposes appreciably. Accordingly, it was found expedient to fuse the test samples, not with pure ferric chloride, but with solutions of ferric chloride in alkali metal chlorides.

Preparation of Melts of Ferric Chloride with Alkali Metal Chlorides

Anhydrous ferric chloride free from $FeCl_2$ was prepared by chlorination of Armco iron at 450 – 500 deg. Subsequently $FeCl_3$ was fused with the chlorides of the alkali metals (a eutectic mixture of KCl + LiCl) at 450 – 500 deg in a stream of chlorine.

At concentrations below 5 – 6% of $FeCl_3$ a homogeneous melt having the color of strong tea was obtained. At higher concentrations, a second liquid phase separated out on the bottom of the test tube.

Table 1 contains results of several experiments in which a eutectic mixture of lithium and potassium chlorides was fused with 10 and 30% of $FeCl_3$ at 500 deg. The fused salts were kept in a liquid state in a chlorine atmosphere for about 5 minutes, and then rapidly cooled. The top and bottom layers which differed sharply from each other in color were analyzed for their contents of $FeCl_3$ and $FeCl_2$ (Table 1).

TABLE 1

$FeCl_3$ added, in % wt.	Found, in % wt.			
	In the top layer		In the bottom layer	
	$FeCl_3$	$FeCl_2$	$FeCl_3$	$FeCl_2$
10	5,1	0,12	65,0	None
10	5,74	0,10	65,3	"
30	6,2	0,11	65,3	"

As the results show, the bottom layer of the fused salts is a phase with a constant composition approximating to that of the compound $KFeCl_4$. The fusion temperature of this phase was 260 ± 2 deg. Microscopic examination showed that no crystals of $FeCl_3$, KCl, or LiCl were present in the congealed lower layer of the fused salts. Obviously, this phase is a solution of KCl in $KFeCl_4$. The yellow anisotropic crystals which made up this phase had a refractive index $n > 1.567$. The top layer of the fused salts was a saturated layer of $KFeCl_4$; after cooling, individual crystals of a second phase of $KFeCl_4$, LiCl, and KCl were found in it under the microscope. It should be pointed out that formation of layers was only observed in the fused mixtures of $FeCl_3$ with LiCl +

KCl; it did not occur in the systems: $FeCl_3$ + NaCl [4], $FeCl_3$ + LiCl, and $FeCl_3$ + KCl (we studied the last two systems). Ferrous chloride which is formed as the result of partial thermal dissociation of $FeCl_3$ concentrated only in the top layer of the melt. This shows that $FeCl_2$ does not dissolve in $KFeCl_4$.

The compound $KFeCl_4$ is more stable to thermal dissociation than ferric chloride. This confirms experiments in which $KFeCl_4$ was held for a definite time in a fused state at 500 deg under an atmosphere of pure argon, and, after rapid cooling, was analyzed for its content of ferrous chloride. Results of these experiments are shown in Table 2; for comparison, results of experiments with a melt containing 8% wt of $FeCl_3$ are included.

As these results show, $FeCl_3$ dissolved in the melt KCl + LiCl broke down more rapidly.

Nevertheless, keeping melts containing ferric chloride for a long time at high temperatures can lead to formation of appreciable amounts of $FeCl_2$, and can therefore lead to incorrect results.

TABLE 2

$KFeCl_4$		Melt, containing 8% wt. of $FeCl_3$ in KCl + LiCl			
Time for which melt was kept at 500°, in min.	$FeCl_2$ found in % wt.	$FeCl_2$ decomposed, in % wt.	Time for which melt was kept at 500°, in min	$FeCl_2$ found, in % wt.	$FeCl_2$ decomposed in % wt.
5	0,006	0,013	4	0,05	0,74
10	0,011	0,022	8	0,06	0,95
15	0,018	0,036	15	0,065	1,02
—	—	—	25	0,10	1,55

When ferric chloride, in the form of the compound $KFeCl_4$ prepared beforehand, is added to the melt in amounts which are only slightly in excess of that required for oxidizing lower valency titanium, and the melt is then rapidly cooled, it is possible to reduce the formation of $FeCl_2$ to a minimum.

Determination of the Amount of Di- and Trivalent Titanium. Below is given a brief description of a method for the determination of di- and trivalent titanium in fused chloride electrolytes.

A sample of the melt was taken and cooled in an inert atmosphere (argon) and then transferred to a Γ-shaped tube. Some $KFeCl_4$ prepared beforehand was placed in a sideshoot of this tube; the amount of $KFeCl_4$ taken should not be more than 1.5 to 2 times the amount necessary for complete oxidation of Ti^{II} and Ti^{III} to Ti^{IV}. The tube was then hermetically sealed, evacuated and filled with pure argon, and its lower end — containing the test material — placed in the heating oven. The sideshoot containing the $KFeCl_4$ should be outside the oven in a cold zone. After the sample had fused, the $KFeCl_4$ was thrown into it by inclining the tube; the tube was then vigorously shaken in order to mix the contents; after mixing the tube was withdrawn from the oven and cooled as rapidly as possible to room temperature. The sample was weighed and dissolved in water, the solution was acidified with H_2SO_4 or HCl (10%). Ferrous iron was determined in the aqueous solution (in mg equivalents per g of sample taken).

TABLE 3

No. of replicates	Ti^{2+} % wt., determined by fusion with Fe^{3+} according to equation (1)	Ti^{3+} % wt., calculated by means of equation (2) on the basis of the fusion reaction	Ti_{total} % wt., calculated as the sum of di- and trivalent titanium	Ti_{total} % wt., determined by dissolution in water and by titration with $FeCl_3$	Relative error, in %
1	4,95	0,67	5,62	5,62	0,04
2	4,92	0,71	5,62	5,62	0,07
3	4,88	0,74	5,62	5,62	0,09
4	2,23	—	2,23	2,23	0,09
5	2,23	—	2,23	2,23	0,09

A second sample was taken from the test melt, and, after cooling to room temperature in an inert atmosphere, was dissolved in dilute H_2SO_4 or HCl (10%). Trivalent titanium (in mg equivalents per g of sample taken) was then determined in the aqueous solution.

Assume that n mg. equivalents of Fe^{II} was found per g of test sample by fusion with $FeCl_3$, and that m mg. equivalents of Ti^{III} per g of sample was found in the aqueous solution, then the original melt will contain:

$$a = 11{,}88\,(n - m)\ \text{Wt. \%}\ TiCl_2. \quad (1)$$

$$b = 15{,}43\,(2m - n)\ \text{Wt. \%}\ TiCl_3. \quad (2)$$

As examples, Table 3 contains results of the analysis of chloride melts, in which titanium was introduced by electrolysis with an anode consisting of titanium oxide (TiO), or by the interaction of dry hydrogen chloride with the metal in the melt.

SUMMARY

1. A method is described for obtaining melts of $FeCl_3$ with alkali metal chlorides, in which thermal decomposition of ferric chloride is reduced to a minimum.

2. A technique is described for the separate determination of di- and trivalent titanium in salt melts by means of ferric chloride which is added to a sample of the test melt in the form of the compound $KFeCl_4$ prepared beforehand.

LITERATURE CITED

[1] S. F. Belov and D. N. Ivanova, Factory Labs. 12, 1415 (1956).

[2] E. G. Tabakova and Z. V. Solov'eva, Factory Labs. 12, 1417 (1956).

[3] J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, 14, London 50-51 (1935).

[4] H. F. Johnstone, H. C. Weingarther, E. Warren and Wishe, J. Amer. Chem. Soc. 64, 241 (1942).

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DETERMINATION OF SMALL AMOUNTS OF ZIRCONIUM AND HAFNIUM IN SILICATE ROCKS

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All rocks and minerals which contain zirconium usually contain hafnium as well [1 – 2]. As a result of of the extremely close similarity in the chemical properties of these two elements, sufficiently accurate methods for their quantitative separation are not yet known. As a result of this they are separated together, and the content of each element in the concentrates thus obtained, is determined either by optical spectroscopy [3], or by X-ray spectrographic methods [4].

All the same, during the separation of zirconium and hafnium from silicates rocks by published methods, it has been found that complete separation of the elements is not achieved by any of these methods, when the total content of zirconium and hafnium is less than 0.01%. Evaluation of the applicability of each of the methods for separating zirconium and hafnium from silicate rocks was carried out as follows. To a finely ground sample of granite free from zirconium and hafnium, was added a known amount of a solution of one of the elements and the requisite amount of a solution of the radioisotope of the same element; the mixture was then broken down with a mixture of hydrofluoric and sulfuric acids (or with a mixture of hydrofluoric and perchloric acids). From the solutions obtained in this way, zirconium and hafnium were precipitated as phosphates, arsenates, mandelates, phenylarsonates, and 4-dimethylaminoazobenzene-4^1-arsonates. The precipitates were calcined and completeness of separation of zirconium and hafnium checked radiometrically. It follows from the results obtained that for a total content of zirconium and hafnium in the tested silicates less than 5×10^{-2}%, their separation in the form of phosphates and arsenates is already incomplete. Quantitative separation of zirconium and hafnium as mandelates under the conditions recommended by Mills and Herman [5] is only possible for a total content of both elements in the silicate rocks of not less than 2×10^{-2}%.

Precipitation with phenylarsonic acid according to the technique developed by Alimarin and Medvedeva [6] ensures complete separation of zirconium and hafnium from silicate rocks containing not less than 1×10^{-2}% of the total.

Decomposition of the sample with a mixture of HF and $HClO_4$ instead of HF and H_2SO_4, and the use of hydrochloric acid for dissolving the residue after decomposition instead of sulfuric acid, favors more complete deposition of the phenylarsonates of zirconium and hafnium. It was also found that by simply increasing the amount of added phenylarsonic acid, it is possible to ensure complete separation of both elements for their total content in silicate rocks of down to 1×10^{-4}%, even from sulfuric acid solutions. All the same, the concentration of zirconium and hafnium achieved under such conditions still proved insufficient (Table 1), as a result of which, the zirconium in the concentrates obtained, in view of its low content, was determined by the X-ray spectrographic method with a large error, while hafnium could not be detected at all. The use of an X-ray spectrographic method for determination of zirconium and hafnium in the concentrates obtained has the advantage that the experimental accuracy in the given instance is independent of the bulk composition of the sample (as is true in optical spectroscopy). The technique applied [4] permits determination of zirconium and hafnium, for contents of these elements in the test sample greater than 0.5 and 0.05% respectively. 3 – 5 mg of test concentrate is sufficient for a determination.

TABLE 1

Composition of the Concentrates Obtained After Calcining Phenylarsonate Precipitates. Sample of Rock 7 – 10 g (according to X-ray spectrographic results)

Element	Content (in %) in the concentrate		Element	Content (in %) in the concentrate	
	After the first precipitation	After the second precipitation		After the first precipitation	After the second precipitation
Ti	>10	>10	Ca	0,1—0,5	Not detected
Zr	0,5—1,5	0,7—2	Ba	0,1	»
Fe	0,1—1	0,1—0,5	Zn	0,007—0,08	0,007—0,01
Al	0,1—1	0,05—0,1	Cu	0,005—0,01	0,005
As	0,1—1,5	0,1—1	Mn	0,001—0,005	0,005
Pb	0,1—1	0,001—0,005	Sn	0,001—0,005	Not detected
Mg	0,1	Not detected	Hf	Not detected	»

Repeated reprecipitation with phenylarsonic acid makes it possible to lower the weight of the concentrate separated from 10 g of silicate rock from 50 – 70 to 38 – 50 mg. The zirconium content after reprecipitation amounts to 0.7 to 2.0%; the hafnium content, however, still cannot be determined with sufficient accuracy (Table 1).

TABLE 2

Distribution of Hf^{181} During the Concentration of Zr and Hf from Silicate Rocks

Content in the rock, in %		Hf^{181} found, as a % of that introduced		
Zr	Hf	In the first filtrate	In the second filtrate	In the concentrate
$1{,}4 \cdot 10^{-2}$	$3{,}0 \cdot 10^{-4}$	0,8	2,0	97,2
$1{,}2 \cdot 10^{-2}$	$2{,}8 \cdot 10^{-4}$	0,4	1,3	98,2
$8{,}4 \cdot 10^{-3}$	$1{,}9 \cdot 10^{-4}$	1,6	3,7	94,5
$3{,}3 \cdot 10^{-3}$	$1{,}0 \cdot 10^{-4}$	1,6	1,8	96,6
$2{,}6 \cdot 10^{-3}$	$5{,}5 \cdot 10^{-5}$	1,5	4,7	94,0

When the concentrate obtained by precipitation with phenylarsonic acid is repeatedly reprecipitated by means of 4-dimethylaminoazobenzene-4^1-arsonic acid, which forms less soluble precipitates with zirconium and hafnium [7 – 9], it is possible, under suitable chosen conditions, to decrease the weight of the concentrate to 3 – 5 mg; the zirconium content of such a concentrate increases to 10 – 66%, while that of hafnium becomes 0.2 – 1.5%. The distribution of Hf^{181} during the concentration of zirconium and hafnium from silicate rocks by the procedure outlined below is shown in Table 2.

The distribution of Zr^{95} during concentration of zirconium and hafnium from the same rocks is identical to the distribution of Hf^{181}; of the Zr^{95} introduced, on an average, 96.8% was found in the concentrates isolated.

The concentration technique consists of the following. 5 – 10 g of finely ground rock is decomposed in a platinum basin with a mixture of hydrofluoric and perchloric acids (or with a mixture of hydrofluoric and sulfuric acids). After the sample has been broken down completely and Hf has been removed, the residue is dissolved in 50 ml of 2 N HCl and the normality of the acid lowered to 1 N by dilution with water; 1 – 2 ml of 30% hydrogen peroxide is added (for masking titanium) followed by 5 – 6 ml of a 20% solution of phenylarsonic acid to precipitate zirconium and hafnium. The precipitate should be allowed to stand for at least 24 hours before filtering, it is then washed with a 0.1% solution of phenylarsonic acid in 0.1 N HCl, and dried, and finally calcined for 1.5 – 2 hours at 900 – 1000 deg. The dioxides of zirconium and hafnium obtained by calcining their phenylarsonates are fused with potassium pyrosulfate, and the melt dissolved in 50 ml of 6 N HCl; the whole is

heated on a water bath for 10 – 15 minutes. After cooling, 1 – 2 ml of 30% hydrogen peroxide is added, followed by 5 ml of a 2% solution of sodium 4-dimethylaminobenzene-4^1-arsonate, 30 – 35 ml of water, and 10 ml of 1% methyl orange solution, which is one of the components of the organic coprecipitant [10] favoring more complete separation of zirconium and hafnium. Instead of methyl orange one can use any sulfonic acid which has a sufficiently high molecular weight, for example, β-naphthalenesulfonic acid, α-anthraquinonesulfonic acid, etc. After 24 hours, the precipitate formed is filtered, washed 2 – 3 times with a 0.1% solution of 4-dimethylaminobenzene-4^1-arsonic acid in 0.1 N HCl, dried, and then calcined at 900 – 1000 deg. The zirconium and hafnium content of the concentrate obtained in this way is determined by an X-ray spectrographic method.

The use of the radioactive isotopes Zr^{95} and Hf^{181} for establishing the completeness of the separation of zirconium and hafnium from silicate rocks, has shown that fairly complete separation of both elements is possible when their total content in the rocks is not less than 1×10^{-4}%.

The method which has been developed has been tested for separating zirconium and hafnium from rocks of the Verkh-Isetskii intrusion, for subsequent X-ray spectrographic determination of each of these elements [11].

In conclusion, we should like to thank I. D. Shevaleevskii for carrying out all determinations of zirconium and hafnium in the concentration obtained by the X-ray spectrographic method.

SUMMARY

A method has been developed for concentrating zirconium and hafnium from silicate rocks containing a total amount of these elements ranging from 0.5 to 1×10^{-4}%. The method consists of their precipitation with phenylarsonic acid, and subsequent reprecipitation with 4-dimethylaminoazobenzene-4^1-arsonic acid. Recovery of each element is 94 – 100%. As a result of this high degree of concentration, it is possible to determine the content of each element with reasonable accuracy by the X-ray spectrographic method.

LITERATURE CITED

[1] D. Coster and G. Hevesy, Nature 111, 182 (1923).

[2] G. Hevesy and R. Hobbie, Z. anorgan. Chem. 212, 142 (1933).

[3] G. Kriuger, R. R. Shvangiradze and T. A. Mozgovaia, J. Anal. Chem. 10, 20 (1955).*

[4] A. S. Pavlenko, E. G. Vainshtein and N. D. Shevaleevskii, Geochemistry 351 (1957).

[5] E. C. Mills and S. E. Herman, Analyst 78, 256 (1953).

[6] I. P. Alimarin and O. A. Medvedeva, Factory Labs. 11, 254 (1945).

[7] F. Feigl, P. Krumholz and E. Rajmann, Microchemie 9, 395 (1931).

[8] V. A. Nazarenko, J. Appl. Chem. 10, 1696 (1937).

[9] W. G. Hayes and E. W. Janes, Ind. Eng. Chem., Anal. Ed. 13, 603 (1941).

[10] V. I. Kuznetsov, J. Anal. Chem. 9, 199 (1954).*

[11] I. M. Lipova, I. D. Shevaleevskii and A. M. Tuzova, Geochemistry, 133, (1957).

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* Original Russian pagination. See C.B. Translation.

PHOTOMETRIC DETERMINATION OF GERMANIUM BY MEANS OF 9-[p-(N-DIMETHYLAMINO)] -PHENYL-2, 3, 7-TRIHYDROXY-6-FLUORONE

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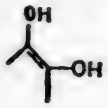
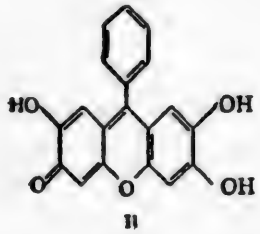
Among those organic reagents known at present for germanium, an important place is occupied by compounds containing the ortho-dihydroxy group [1] in their molecules



The most interesting of such organic compounds is 9-phenyl-2, 3, 7-trihydroxy-6-fluorone (II), which was suggested for the determination of germanium by Giles in 1947 [1].



II

Thanks to its high sensitivity and specificity, phenylfluorone has found wide application in the analytical chemistry of germanium.

On addition of traces of germanium to solutions of phenylfluorone in dilute hydrochloric or sulfuric acid, there is observed a change in the color of the solution from yellow to orange, as a result of the separation of the raspberry-colored precipitate of the germanium-phenylfluorone compound.

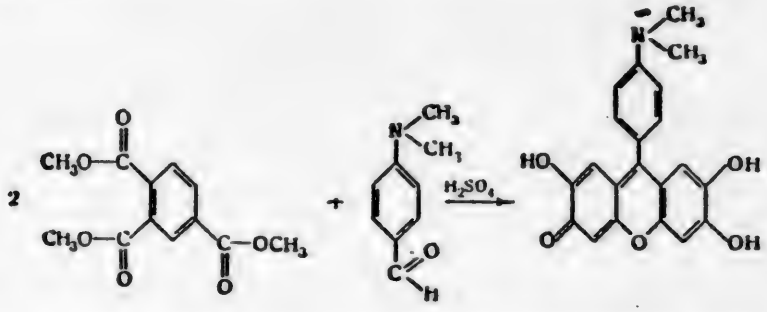
The fact that the product formed by the interaction of germanium with phenylfluorone separates out as a solid phase presents serious difficulties for the use of this reagent for the photometric determination of germanium, such a determination being, accordingly, only possible in the presence of stabilizing agents in solution. Thus, Cluley [2] using gum arabic managed to prepare stable sols of the phenylfluorone compound of germanium with contents of up to 20 γ of GeO_2 in 1 ml of solution. Cluley's method has not found wide application in the Soviet Union because of the nonavailability of gum arabic. Attempts have been made to use gelatine instead of gum arabic [3]. Using gelatine, we were only able to get stable sols of the germanium-phenylfluorone compound in very dilute solutions containing not more than 0.2 γ GeO_2 in 1 ml. In addition, the reproducibility of the color intensity of the solutions proved to be far from satisfactory, particularly in more concentrated germanium solutions, since in the presence of gelatine, even when the conditions used were kept strictly identical, it was difficult to prepare suspensions of the germanium-phenylfluorone compound with equal degrees of dispersion (on which the intensity and shade of the color of the solution mainly depends).

It would be more expedient to change the properties of the reagent itself in such a way that the product obtained, while preserving the sensitivity and specificity of phenylfluorone, formed soluble compounds with germanium. One approach to solving this problem appeared to be the introduction of basic groups into the phenylfluorone molecule.

In the course of the work described here, an analog of phenylfluorone containing a basic substituent was synthesized, this compound was: 9[p-(N-dimethylamino)]phenylfluorone; conditions were also established for the photometric determination of germanium by this new reagent.

Synthesis of 9-[p-N-dimethylamino)]-phenylfluorone

Synthesis of 9-[p-(N-dimethylamino)] phenylfluorone can be carried out in a similar fashion to that of phenylfluorone, the only difference is the use of N-dimethylaminobenzaldehyde instead of benzaldehyde; p-N-dimethylaminobenzaldehyde is condensed with triacetylhydroxyquinone in the presence of concentrated sulfuric acid according to the scheme:



18 g (0.072 M) of freshly prepared triacetylhydroxyhydroquinone and 5 g (0.035 M) of p-dimethylaminobenzaldehyde are dissolved on heating in a mixture of 80 ml alcohol, 80 ml water, and 8 ml of concentrated sulfuric acid. The solution obtained is boiled on a water bath for 10 hours, and is then kept for 10 hours at room temperature. The orange-red precipitate of the sulfate of 9-[p-(N-dimethylamino)] phenylfluorone which is formed, is filtered off, and then dissolved in a mixture consisting of 80 ml of alcohol, 80 ml of water and 8 ml of concentrated sulfuric acid. The solution obtained is boiled for 5 minutes with a small amount of activated charcoal, after which the charcoal is filtered off, while the hot filtrate is neutralized with ammonia to a pH of approximately 7; a red precipitate of the base 9-[p-(N-dimethylamino)] phenylfluorone thereupon separate out. The latter is filtered while hot, and is washed with hot water until there is complete absence of any smell of ammonia.

9-[p-(N-dimethylamino)]phenylfluorone is a red microcrystalline powder with a greenish tinge, and has a melting point higher than 300 deg; it is insoluble in water and in most organic solvents. It dissolves readily in alkalis to form raspberry-red solutions. It dissolves in mineral acids on heating, or in the presence of alcohol.

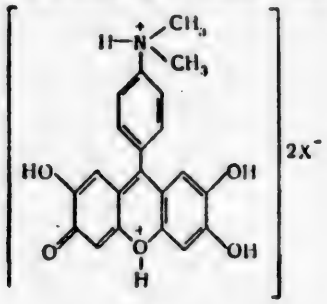
Yield 66 g (52%). Found in %: N 3.73; 3.75. Calculated %: N 3.85.

Henceforth we shall denote 9-[p-(N-dimethylamino)]phenylfluorone by DAPhF, while its compound with germanium will be denoted by germanium-DAPhF compound.

Photometric Determination of Germanium by Means of 9-[p-N-dimethylamino)]-phenylfluorone

Conditions for the photometric determination of germanium by means of DAPhF were established for the case of hydrochloric acid solutions, since such solutions are prepared in the course of analysis. DAPhF forms salts with acids by means of their amino- and oxonium groups (III). The most stable solutions of DAPhF were those obtained in the case of dilute hydrochloric acid solutions (C < 1N); in more concentrated hydrochloric acid solutions, on standing, a yellow crystalline precipitate separated out, presumably, as the result of the formation of a sparingly soluble salt through the oxonium oxygen. In weakly acid media, the possibility of the formation of oxonium salts is limited on account of the greater tendency to hydrolyze, and DAPhF is kept in solution thanks to the readily soluble salt it forms through the amino nitrogen. With increasing temperature, the stability of DAPhF

solutions increases because of the increasing solubility of its oxonium salt.



III

In the presence of germanium, the yellow color of DAPhF solutions changes to orange; under these conditions, the maximum of the color intensity is only observed on addition of a large excess of reagent. This indicates a low stability for the germanium – DAPhF compound formed, this being determined, presumably, by an increase in the basic properties of the reagent as a result of the introduction of the basic amino group into its molecule.

It has been established that maximum color stability of the solutions of the germanium-DAPhF compound is achieved on addition of 2 ml of a 0.5% solution of DAPhF per 8 ml of the test solution containing from 0.5 to 1.0 γ of GeO_2 in 1 ml.

Solutions of the germanium-DAPhF compound show an appreciable opalescence when examined in ultraviolet light-this indicates their colloidal character; nevertheless, the presence in the molecule of the compound of a basic dimethylamino group communicates to the sols stability in acid media.

In dilute hydrochloric acid (1 N), solutions of the compound of germanium with DAPhF, for contents of the germanium of 1.2 γ GeO_2 in 1 ml, are stable enough without addition of any stabilizing agents. With increasing acidity of the solution, the stability of the sols of the germanium-DAPhF compound decreases as the result of the formation of the oxonium salt.

Solutions of the germanium-DAPhF compound are highly dispersed colloïdal systems and fully conform to the Lambert – Beer law at low germanium concentrations (c < 1γ GeO_2/ml). The deviations from this law which are observed at higher germanium concentrations, are related, apparently, to a decrease in the dispersivity of the system (Fig. 1).

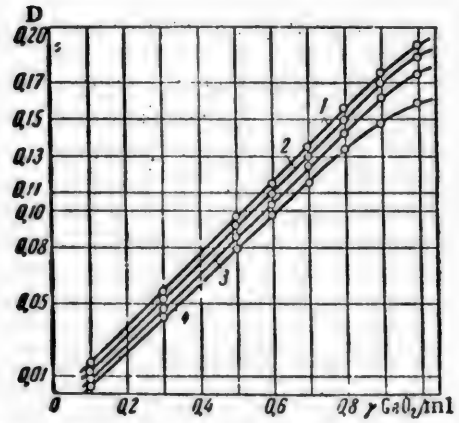


Fig. 1. Relation between the optical density of solutions of the germanium – DAPhF compound and the germanium concentration: 1) in 0.2 N HCl; 2) in 0.5 N HCl; 3) in 0.7, 0.9, 1.0 and 1.1 N HCl; 4) in 1.18 N HCl (t = 22 deg).

The curves shown in Fig. 1 show that the value of the optical density of solutions of the germanium – DAPhF compound falls with increasing acidity of the medium.

Temperature affects the value of the optical density of the colored compound of germanium (Curves in Fig. 2); with decreasing temperature the value of the optical density of solutions of the germanium – DAPhF compound increases appreciably. Changes in the color of solutions of the germanium – DAPhF compound, determined by temperature variations, are completely reversible: on returning to the original temperature conditions, the intensity of the color of the solutions is rapidly and completely restored.

At a constant temperature, the color of solutions of the germanium – DAPhF compound in weakly acid media remains stable for several hours. The maximum color intensity is obtained in 0.5 – 1.5 hours, depending on the acidity of the solution (Fig. 3).

Measurements of the optical density of the solutions were carried out on a FEK-M photocolorimeter using a green filter having a transmission region at 600 – 580 mμ.

The sensitivity of the determination amounts to 0.05 γ GeO_2 in 1 ml of test solution.

Arsenic and bismuth present in the solutions being photometrically measured have no effect on the germanium determination. Under similar conditions, antimony (III), tin (IV), and molybdenum react with DAPhF, but the sensitivity of the reagent with these elements is appreciably less than with germanium.

As the result of work we carried out, a technique has been developed for the photometric determination of small amounts of germanium by means of DAPhF; the procedure is given below.*

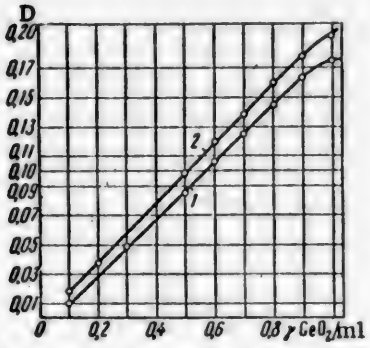


Fig. 2. Effect of temperature on the optical density of solutions of germanium – DAPhF compound 1) 23°; 2) 16°.

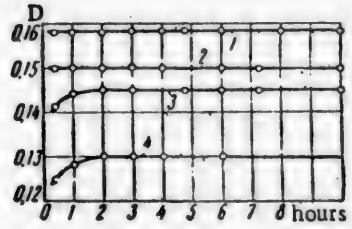


Fig. 3. Change in the optical density of solutions of the germanium–DAPhF compound with time: 1) in 0.2 N HCl; 2) in 0.5 N HCl; 3) in 0.75 N HCl; 4) in 1.2 N HCl.

Experimental Procedure. The test hydrochloric acid solution of germanium was adjusted to 0.75 – 1 N by addition of the necessary amount of water or HCl. From the hydrochloric acid solution prepared in this way, 8 ml of the solution was pipetted into a small graduated tube, the germanium content in the given volume being less than 10 γ GeO_2. When the test solution contained more germanium, a smaller aliquot was taken and the volume made up to 8 ml with 0.9 N HCl. 2 ml of a 0.05% solution of DAPhF was added and the whole mixed and left to stand in the dark for one hour.**

The optical density was measured with a green filter, using a cell with a layer thickness of 10 mm. The reference solution was an identical solution containing all the reagents apart from germanium. The germanium content was established by means of a calibration curve.

A calibration curve was constructed by measuring out from 0.1 to 1 ml of a stock solution of germanium containing 10 γ GeO_2 in 1 ml, into test tubes, and making the volume up to 8 ml with 0.9 N HCl in each case. 2 ml of reagent solution was added to each test tube, and, after standing for one hour, the optical density was measured.

It is essential that the construction of a calibration curve and determination of germanium should be carried out under the same temperature conditions.

The authors wish to thank N. Ia. Postovskii for his valuable advice during the work described here.

SUMMARY

The synthesis of 9-[p-(N-dimethylamino)]phenyl-2, 3, 7-trihyroxy-6-fluorone – a reagent for germanium – is described. The advantages of 9-[p-(N-dimethylamino)]phenylfluorone over phenylfluorone is that solutions of the germanium compound of the former are stable in acid media, for germanium contents up to 1.2 γ GeO_2 per ml, and that this reagent can be used for photometric determination of germanium without having to use special stabilizing agents. A method has been developed for the photometric determination of germanium using the reagent mentioned above.

* After completion of the work described here we became aware, via a reference article, of an article by some Japanese workers: Kenjero Kimura, Kazuo Saita, Masaka Asada published in Chem. Abstracts 51, No. 1, 125 (1957), in which 9-[p-(N-dimethylamino)]phenylfluorone was described as a reagent for germanium. Information regarding the use of this compound for the quantitative determination of germanium was not given in the reference.

** Preparation of DAPhF solution: 0.5 g of the reagent was dissolved in 50 ml of 0.9 N HCl on heating at 60–70 deg, and the volume made up to 100 ml with alcohol.

LITERATURE CITED

[1] J. Giles, S. Histe and A. Clayes, Analyt. chem. acta, 9, 302 (1947).

[2] H. Cluley, Analyst 76, 523 (1951).

[3] V. Nazarenko, N. Lebedeva and R. Ravitskaia, Factory Labs. 24, 9 (1958).

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DETERMINATION OF VANADIUM AND CHROMIUM BY PHOTOMETRIC TITRATION

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The method most widely used for the determination of vanadium and chromium in alloyed steels, and of vanadium in ferrovanadium, is titration with Mohr's salt using phenylanthranilic acid as indicator [1]. Nevertheless, during the determination of vanadium in steels containing large amounts of chromium or nickel, visual fixing of the endpoint becomes difficult and demands considerable experience on the part of the analyst. In this connection, therefore, worthy of attention is the use of a selenium photoelement in conjunction with a sensitive galvanometer, as an apparatus which permits more accurate registration of the endpoint.

Gaukhman, Reznik, and Ginsburg [2] who substituted visual observation of the change in color of the indicator by a photoelectric method, used the method of photometric titration for the determination of vanadium and chromium in alloyed steels.

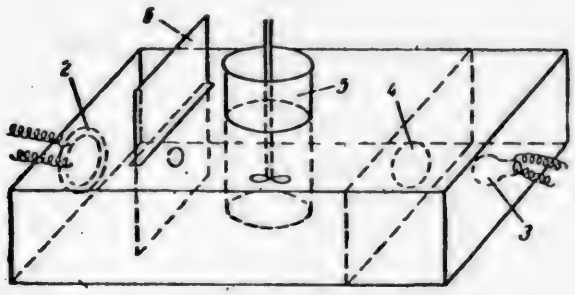

Fig. 1.

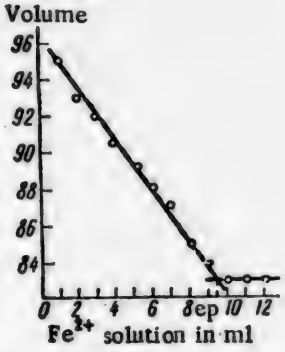

Fig. 2.

Fig. 1. Titration photocolorimeter: 1) Plywood box 24 × 11 × 7 cm; 2) selenium photoelement; 3) 6 volt lamp , 4) condensing lens; 5) cell; 6) diaphragm.

Fig. 2. Titration curve of 10 mg of vanadium with 0.02 N Fe^{2+} solution on the basis of the characteristic color formed; e.p. equivalence point.

Miles and Englis [3] used changes in the characteristic color of quinquevalent vanadium and of dichromate ions, under the action of a reducing agent, for the determination of chromium and vanadium in steels, by a spectrophotometric titration method. The method, according to the authors, gives satisfactory results, but requires preliminary separation of vanadium and chromium.

The present article contains a description of a simple method for the determination of chromium and vanadium in alloys by photometric titration in which a photocolorimeter of simple design is used.

The apparatus is shown schematically in Fig. 1. The light source is a 6 volt automobile lamp fed from an accumulator. The receiver for the light energy is a selenium photoelement. The titration cells are normal 100

ml chemical beakers. Agitation of the solution being titrated is carried out by means of an electrically driven glass stirrer which is kept in the beaker during the whole of the titration. The recording apparatus is a needle galvanometer with a scale divided into 100 divisions, $1^{\circ} = 0.75 \times 10^{-6}$ amps, R = 189 ohm. In order to attenuate the light flow passing through weakly colored solutions, sheets of thick black paper with openings of different diameter are used; the diaphragms are placed in a slit in the upper cover of the apparatus between the cell and the photoelement. The volume of the liquid can be varied within the limits 60 – 80 ml during titration.

TABLE 1

Results of Determination of Vanadium in Ferrovanadium (standard sample 77 a)

As determined by photometric titration, in %	As determined by titration using phenylanthranilic acid as indicator, in %
47.25	47.42
46.04	45.88
46.21	46.10
46.16	45.96

For carrying out a titration, the beaker containing the test solution is placed in the housing of the photocolorimeter, and a diaphragm is chosen so that the galvanometer needle is located towards the end of the scale (90 – 100 divisions); the motor is switched on and the solution titrated with a solution of Mohr's salt; the galvanometer reading (n-divisions) is noted after addition of each aliquot of solution.

The method suggested is based on the reduction of quinquevalent vanadium to the quadrivalent state by Mohr's salt, this reduction being accompanied by the appearance of a blue color. During titration, the galvanometer needle gradually returns to the lower scale divisions, and, after reaching the equivalence point, remains constant.

Typical titration results are shown graphically in Fig. 2. The optimum amount of vanadium in the solution being titrated is 5 – 10 mg. Chromium, nickel, and molybdenum do not interfere with the determination of vanadium under these conditions.

Determination of Vanadium in Ferrovanadium.* 0.05 g of ferrovanadium is dissolved on heating in 5 ml of H_2SO_4 (1:3) contained in a 100 ml beaker, and the heating continued for another 1 – 2 minutes. The solution is cooled and diluted with water to 60 – 70 ml, and $KMnO_4$ solution added dropwise until a stable rose color is obtained; excess permanganate is destroyed by addition of a saturated solution of oxalic acid. The beaker is placed in the photocolorimeter and titrated with a 0.02 N solution of Mohr's salt, the latter being added in 2 – 4 ml aliquots initially and then, after addition of about 12 – 14 ml, added in 1.0 ml lots until the galvanometer gives a constant reading. The solution of Mohr's salt is standardized against a standard sample of ferrovanadium.

TABLE 2

Results for the Determination of Vanadium in Steels not Containing Tungsten

Steel, standard sample no.	Certified content of V, in %	Found by photometric titration, in %	Absolute deviation, in %
30	0.26	0.26	±0.00
30v	0.29	0.29	±0.00
		0.28	−0.01
107	0.30	0.32	+0.02
		0.30	±0.00
124a	0.15	0.15	±0.00
		0.16	±0.01

Table 1 contains results obtained for the determination of vanadium in ferrovanadium by photometric titration. For comparison, the Table also contains results obtained during determination of vanadium by visual titration using phenylanthranilic acid as indicator. The time taken for a titration is 5 – 8 minutes.

Determination of Vanadium in Steels not containing Tungsten. To 1.0 – 3.0 g (depending on the vanadium content) of steel is added 30 ml of water and 25 ml of a mixture of acids (15 ml H_2SO_4 sp. gr. 1.84 and 10 ml of H_3PO_4 sp. gr. 1.7). The sample is dissolved initially at room temperature and subsequently on heating. After the sample has dissolved, carbides are destroyed by addition of 0.5 ml of concentrated nitric acid; the procedure subsequently followed is the same as that described for the analysis of ferrovanadium. Results of such vanadium determinations are given in Table 2.

Determination of Vanadium in Steels in the Form of the Phosphotungstovanadium Complex. When tungsten is present in steels, it is possible to carry out photometric titration by making use of the capacity of the phosphotungstovanadium complex to color the solution a dark-

* E. Zimina and I. Iakusheva participated in the experimental work.

violet when the former is reduced by Mohr's salt. During titration of vanadium solutions in the presence of tungsten and phosphoric acid, the light absorption of the solution increases very insignificantly, and only near the equivalence point is there observed a sharp increase in light absorption as the result of the reduction of the phosphotungstovanadium complex; this stage corresponds to displacement of the galvanometer needle towards zero on the scale (Fig. 3). The jump, and also the slope of the straight line on the graph depend on the vanadium content of the solution. Molybdenum does not affect the position of this jump, since at sulfuric acid concentrations greater than 1.6 N, the phosphomolybdate complex breaks down [4]. Apart from the fact that this phenomenon facilitates the problem of determining vanadium in high-speed steels, it also permits the amount of sample necessary for the analysis of steel not containing tungsten to be reduced. In such cases sodium tungstate is added to the solution prior to titration.

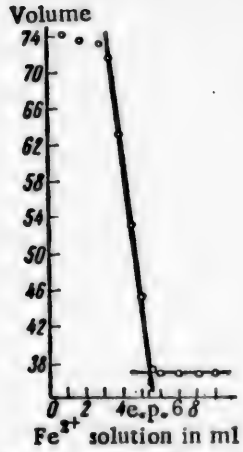

Fig. 3. Titration curve for 3 mg of vanadium with 0.01 N Fe^{2+} solution in the presence of tungsten and phosphoric acid; e.p. — equivalence point.

1.0 g of steel (for vanadium contents of 0.15 — 0.30%), 0.5 g of steel (for vanadium contents of 0.3 — 1.0%), or 0.2 g (for vanadium contents of 1.0 — 1.9%) is dissolved in 15 ml or 10 ml, respectively, of acid mixture (50 ml water, 50 ml H_2SO_4 sp. gr. 1.84, and 50 ml H_3PO_4 sp. gr. 1.7) on heating. After solution is complete, carbides are destroyed with nitric acid, the solution is then cooled and diluted with water to 60 — 70 ml, and, where the steel does not contain tungsten, 5 ml of a 0.05 N solution of sodium tungstate added (an aliquot of sodium tungstate is dissolved in the minimum amount of 0.5 N sodium hydroxide and the solution acidified to the congo-red endpoint with phosphoric acid; the requisite amount of water is then added); the vanadium is oxidized with permanganate solution and excess of the latter destroyed with oxalic acid. The beaker is placed in the photocolorimeter and titrated with 0.02 or 0.01 N Mohr's salt solution; the latter is added initially in 2 — 3 ml lots, and near the equivalence point in 0.2 — 0.1 ml lots; after 3 — 4 points have been obtained, the Mohr's salt solution is added in 0.5 — 1.0 ml lots until the galvanometer gives a constant reading.

The results obtained are given in Table 3.

Determination of Vanadium and Chromium in Steels on one Aliquot. The method in which the titration endpoint was determined by means of the phosphotungstovanadium complex was found to be applicable for the determination of chromium and vanadium on one aliquot. In this case, the number of mls of Mohr's salt solution used up for titrating total chromium and vanadium is established first; subsequently, by repeated titration, in the solution oxidized by permanganate solution, the number of mls of Mohr's salt solution used up for reducing vanadium alone is determined. Ammonium persulfate in the presence of a cobalt catalyst [5, 6] is used for oxidizing chromium and vanadium.

TABLE 3

Determination of Vanadium in Steels Using the Phosphotungstovanadium Complex

Steel, standard sample no.	Certified content of V, in %	Found by the photometric titration method, in %	Absolute deviation, in %	Steel, standard sample no.	Certified content, of V, in %	Found by the photometric titration method, in %	Absolute deviation, in %
30	0.26	0.26	± 0.00	122	1.85	1.84	−0.01
		0.28	+ 0.02			1.87	+ 0.02
		0.26	± 0.00			1.89	+ 0.04
30v	0.29	0.29	± 0.00	135	0.29	0.29	± 0.00
		0.30	± 0.01			0.28	−0.01
		0.27	−0.02	156	1.50	1.54	+ 0.04
107	0.30	0.29	−0.01			1.48	−0.02
124a	0.15	0.15	± 0.00			1.49	−0.01
		0.16	−0.01	197	1.26	1.23	−0.03
						1.24	−0.02

TABLE 4

Determination of Chromium and Vanadium in Alloyed Steels

Steel, standard sample no.	Certified content of Cr, in %	Cr, found by photometric titration method, in %	Absolute deviation, in %	Certified content of V, in %	V, found by photometric titration method, in %	Absolute deviation, in %
122	4,17	4,19	+0,02	1,89	1,85	−0,04
156	4,66	4,64	−0,02	1,50	1,56	+0,06
197	4,32	4,24	−0,08	1,26	1,29	+0,03

TABLE 5

Determination of Chromium and Vanadium in Production Samples

Mark of sample	Cr, found by phenyl-anthranilic acid method, in %	Cr, found by photometric titration method, in %	Absolute deviation, in %	V, found by phenyl-anthranilic acid method in %	V, found by photometric titration method, in %	Absolute deviation, in %
RF-1 5879	3,99	3,87	−0,12	1,09	1,04	−0,05
RF-1 6925	4,00	4,00	±0,00	1,08	1,12	+0,04
9×2 MF	1,80	1,71	−0,09	0,18	0,19	+0,01
6017	1,80	1,76	−0,04	0,18	0,19	+0,01
	1,80	1,81	+0,01	0,18	0,19	+0,01
15×5 MF	5,04	4,98	−0,06	0,13	0,14	+0,01
6837	5,04	4,96	−0,08	0,13	0,18	+0,05

0.5 g of steel is dissolved in 30 ml of acid mixture (380 ml water, 90 ml H_2SO_4 sp. gr. 1.84, and 60 ml H_3PO_4 sp. gr. 1.7) in a 100 ml beaker. When solution is complete, carbides are destroyed by careful dropwise addition of HNO_3. The solution is evaporated until white fumes of H_2SO_4 appear, hot water is added, followed by 5 ml of 0.05 N tungstate solution (where the steel contains tungsten there is no need to add the tungstate), and 10 ml of the cobalt catalyst (0.5% solution of $CoSO_4 \cdot 7H_2O$) and the whole heated to the boiling point; to the boiling solution is added, carefully, 20 ml of a freshly prepared 25% solution of ammonium persulfate, and boiling continued for 1 − 2 minutes until the raspberry color of permanganate appears; the solution is then kept on a hot plate until the ammonium persulfate has decomposed completely; the solution is boiled again and 10 ml of a 5% solution of NaCl solution added; heating is continued for 5 − 10 minutes after the color of the permanganate has disappeared. The cooled solution is titrated with 0.05 N Mohr's salt solution as described above. When total chromium and vanadium has been titrated, the galvanometer reading becomes constant. Without removing the beaker from the apparatus, the vanadium is oxidized with permanganate, and the vanadium then titrated with 0.05 N Mohr's salt solution.

SUMMARY

A method has been developed for the determination of chromium and vanadium in ferrovanadium and in steels, which is based on photometric titration, and dispenses with the use of an indicator.

The use of the phosphotungstovanadium complex for the determination of chromium and vanadium in high-speed steels excludes the necessity of removing tungsten.

LITERATURE CITED

[1] V. I. Teploukhov, "Express Analysis of Steels," [in Russian] Metallurgizdat, Moscow (1954).

[2] M. S. Gaukhman, B. E. Reznik and G. M. Ginsburg, Factory Labs. 16, 1045 (1950).

[3] J. Miles and D. Englis, Analyt. Chem. 27, 1996 (1955).

[4] A. K. Babko and L. M. Evtushenko, Factory Labs. 23, 423 (1957).

[5] V. I. Kuznetsov and L. M. Budanova, J. Anal. Chem. 8, 54 (1953).*

[6] L. M. Kul'berg, L. A. Molot and L. F. Grigor'eva, J. Anal. Chem. 8, 370 (1953).*

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* Original Russian pagination. See C.B. Translation.

DETERMINATION OF SULFATES BY REDUCTION TO HYDROGEN SULFIDE

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The most widely used method for the determination of sulfates is their gravimetric determination as $BaSO_4$.

Titrimetric methods of determining sulfates, although they take less time than the gravimetric method, have restricted application, particularly for the determination of small amounts. The most interesting methods of determining sulfates are those based on reduction of sulfates to hydrogen sulfide with a subsequent iodometric finish. Apart from significantly accelerating an analysis, the accuracy of the determination can also be increased when this technique is used.

One of the earliest investigations in this direction was the work of Auger and Gabillon [1], who, for the determination of sulfates, reduced them to hydrogen sulfide by means of hydrogen iodide in the presence of phosphoric acid on heating. Lorant [2] for this purpose used a mixture of hydrogen iodide and formic acid to which a small amount of red phosphorus had been added. Roth [3] used the same medium for the reduction, but instead of red phosphorus suggested potassium hypophosphite as a reducing agent. Hypophosphorous acid was used as reducing agent in a number of subsequent investigations. Thus, Pepkovich [4], Gorak [5], and Archer [6] used a mixture of hydrochloric, hydriodic, and hypophosphorous acids for reducing sulfates.

Rancke-Madsen [7] solved the problem of reducing sulfates in another way, he suggested reducing them by stannous chloride in the presence of phosphoric acid. Since, during the reaction, hydrogen chloride is evolved, which interferes with the absorption of hydrogen sulfide by cadmium acetate solution, Kiba, Takagi, Ioshimura, and Kishi [8] suggested as a reducing agent, a reagent obtained by heating stannous chloride with concentrated phosphoric acid for removal of hydrogen chloride.

This method has been used subsequently for the determination of sulfur in organic materials and for the micro determination of sulfates [9 – 11].

When stannous chloride and phosphoric acid are used for the reduction of sulfates, according to Rancke-Madsen, mercury and copper salts interfere; when the reagent "divalent tin – phosphoric acid" is used, according to the results of Kiba et al, copper and other metals of the same analytical group which give sparingly soluble sulfides interfere.

Taking into account the results obtained in previous work, we made a study of the method of determining sulfates by reducing them to hydrogen sulfide by means of the reagent prepared from divalent tin and phosphoric acid.

The reduction apparatus suggested by Kiba and his co-workers has a number of disadvantages. Concentration of the liquid in it by boiling is very difficult, cleaning of the apparatus takes a long time; in addition, despite the fact that the apparatus is made of quartz, phosphoric acid at 300 deg attacks the walls strongly. We modified the reduction apparatus (Fig. 1).

In order to prevent corrosion of the apparatus walls and for simplifying the preparation of test samples for analysis, we carried out the reaction in a quartz round-bottom beaker – a holder; this, in addition, speeds up the work since changing these holders round takes very little time.

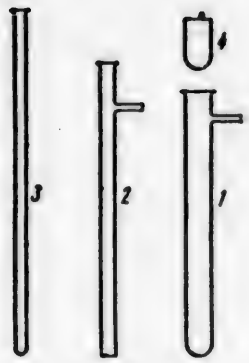

Fig. 1. Details of the reduction apparatus made from transparent quartz: 1) Reaction vessel, about 225 mm long, internal diameter 27 mm; 2) tube for leading in CO_2, about 285 mm long, internal diameter 13 mm; 3) thermometer case, about 340 mm long, internal diameter 8.5 mm; 4) holder, 50 mm long, external diameter 26 mm having a lug on the upper edge, and a mark on the wall corresponding to a volume of 8 ml.

The apparatus (Fig. 2) is assembled by means of rubber stoppers. Flask 6 contains 25 ml of cadmium acetate solution [25 g of $(CH_3COO)_2Cd \cdot 2H_2O$ + 1 ml of CH_3COOH per liter) made up to 80 – 90 ml with water. Flask 7 contains 15 ml of the same solution of cadmium acetate made up to 50 – 70 ml with water, and acidified with 2 ml of CH_3COOH. It is essential to make sure that when the apparatus is being assembled, the lower edge of the tube used for leading in the CO_2 is underneath the upper edge of the holder, but not lower than 8 mm above the surface of the reaction mixture.

The apparatus is set up in an asbestos cover for ensuring more uniform heating of the reaction mixture.

CO_2 prepared in the usual way in a Kipps' apparatus is passed successively through cupric sulfate solution, water, and concentrated H_2SO_4, and then through a calcium chloride tower.

According to the directions given by Kiba et al. the reagent used for reducing sulfates is prepared by heating stannous chloride with concentrated phosphoric acid until all the hydrogen chloride has been removed. We found, however, that when these conditions were observed, the reagent obtained did not have a constant activity. Our observations showed that the small amounts of chlorides remaining in the reagent after evaporation, not only did not interfere with the reduction reaction, but, on the contrary, made it go more intensely. Prolonged heating during preparation of the reagent, in order to remove hydrogen chloride, even without taking the temperature above 300 deg, led to an appreciable drop in its reducing capacity, presumably, as the result of the formation of considerable amounts of pyrophosphoric acid.

The reagent used for reducing sulfates is prepared by heating $SnCl_2 \cdot 2H_2O$ with concentrated phosphoric acid. It is not advisable to use commercial $SnCl_2 \cdot 2H_2O$ for preparing the reagent, since it may be contaminated with sulfates, and, moreover, may also contain some $SnCl_4$. We recommend that the reagent be prepared as follows: 30 g of metallic tin (analytical grade or chemically pure grade) is treated in a 500 ml quartz flask with excess (200 – 300 ml) hydrochloric acid sp. gr. 1.19. The flask is covered with a small funnel and heated on a water bath until the tin dissolves. When this has been effected, the funnel is removed and the flask placed on an electric hot plate and the liquid evaporated while carbon dioxide is passed through the flask, until a crystalline film is formed. The electric hot plate is then removed and replaced by a vessel containing cold water. When this is done the contents of the flask crystallize almost completely, and only a small amount of sirupy liquid may be left. During evaporation of the $SnCl_2$ solution, 1 – 2 small lumps of tin metal should be added to the flask in order to prevent any possible oxidation.

Concentrated phosphoric acid is prepared by heating 300 g of orthophosphoric acid (analytical or chemically pure grade) sp. gr. 1.7 (approximately 170 ml) in a 500 ml quartz flask using a thermometer in a quartz case; the heating is carried out on an electric hot plate and the vapors liberated are sucked through a tube by means of a water pump. Heating is carried out until the temperature has reached 300 deg, after which the still hot flask is placed in a desiccator and cooled over KOH or $CaCl_2$.

Into a quartz flask containing the $SnCl_2$ prepared beforehand, and heated to the point of incipient fusion in its own water of crystallization, is added the slightly warmed, dehydrated concentrated phosphoric acid, and the mixture agitated and heated on an electric hot plate; the temperature is registered with a thermometer in a quartz case and carbon dioxide is passed over the surface while the liquid is being heated. It is desirable that the heating be carried out rapidly; it should be continued until the temperature reaches 300 deg. Usually, heating takes about 25 – 30 minutes. Hydrogen chloride is thereby removed. The temperature should not be taken beyond 300 deg. If, when the temperature reaches 300 deg, small amounts of HCl continue to come off (test by the appearance of NH_4Cl fumes when a stopper with NH_4OH is brought near the neck of the flask), heating is nevertheless discontinued, since the small amounts of hydrogen chloride which still remain at this stage do

not have a deleterious effect on the quality of the reagent obtained, while prolonged heating at 300 does appreciably lower its activity.

The thick sirupy liquid obtained is first cooled in a CO_2 stream (down to 150 deg), and then in a desiccator over KOH or $CaCl_2$ and stored there.

Twice this amount of reagent can be prepared in one lot by doubling the amount of metallic tin and phosphoric acid. During treatment of the $SnCl_2$ with phosphoric acid in this case, heating for removal of hydrogen chloride is continued for a little longer (about 30 – 40 minutes).

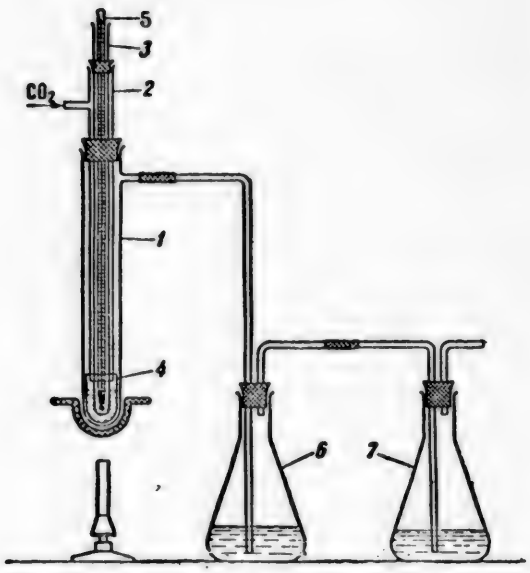

Fig. 2. Apparatus for reducing sulfates: Details 1 – 4 are in Fig. 1; 5) thermometer graduated to 360 deg; 6 and 7) absorption flasks, 200 ml each.

In order to study the reduction of sulfates, an accurately measured amount of standard H_2SO_4 solution was introduced into the quartz holder, and evaporation carried out until the residue is almost dry, reagent is then added, the holder placed in the reduction apparatus and determination carried out as described in the section on "analytical procedure."

As the results given in Table 1 show, fairly consistent results are obtained; the experimental error lies within the limits of a few hundredths of a milligram.

The negative error obtained during determination of large amounts of sulfates, amounting to some tenths of a milligram, depends not so much on incomplete reduction, but on the coating of particles of undecomposed cadmium sulfide by sulfur during the interaction with iodine. This phenomenon is only observed during treatment of large amounts of cadmium sulfide with iodine. During a study of the effect of some of the most common cations, a standard solution of sulfuric acid and a solution of the chloride of one of the metals indicated in Table 2 were measured by means of a pipet into the holder; the holder was then placed on a water bath and the liquid evaporated to dryness. Reagent was then added to the dry residue and the determination carried out as described below.

As the results given in Table 2 show, metals of the second and third analytical groups (Ba, Fe, Al, Cr, Mn, Zn, Co, Ni) do not affect the reduction, and the results obtained are completely satisfactory. Of the elements in the fourth analytical group, Cd, Pb, and Bi do not interfere with the determination. Only bismuth forms a black precipitate of bismuth sulfide during reduction; this precipitate, however, decomposes completely on increasing the temperature further. In the presence of Cu and Hg, the results obtained are very low. In this case the sulfates are also reduced completely, but part of the H_2S formed combines to form the very stable sulfides of copper and mercury which are not completely decomposed under the conditions used for the reaction.

The presence of small amounts of chlorides, of the order of 0.1 g in the test sample, favors a more intensive reduction reaction. The amount of cadmium acetate in the receiver ensures a sufficient buffering capacity to suppress the effect of hydrogen chloride driven into the receiver on the deposition of cadmium sulfide. The presence of too large amounts of chlorides may give rise to such conditions that, as a result of increased acidity in the first absorption flask, the liberated hydrogen sulfide will not be bound by the cadmium and will break through into the second flask, and thus give rise to partial losses. Accordingly, when large amounts of chlorides are present, it is essential to remove some of them by evaporation on a sand bath with a few drops of dehydrated phosphoric acid at 140 – 150 deg.

As was to be expected, even insignificant amounts of nitrates interfered; they must be removed by repeated evaporation with hydrochloric acid on a water bath.

Results for the determination of sulfates in natural materials (natural gypsum and Black Sea slime) are given in Table 3.

TABLE 1

S taken, in mg	S found, in mg	Error, in mg	S taken, in mg	S found, in mg	Error, in mg
11,20	11,11	−0,09	0,80	0,81	+0,01
11,20	11,08	−0,12	0,80	0,78	−0,02
8,00	7,92	−0,08	0,32	0,34	+0,02
8,00	7,95	−0,05	0,32	0,31	−0,01
4,00	4,00	±0,00	0,16	0,17	+0,01
4,00	3,99	−0,01	0,16	0,16	±0,00
1,60	1,63	+0,03	0,08	0,08	±0,00
1,60	1,59	−0,01	0,08	0,09	+0,01

TABLE 2

Taken, in mg		S found, in mg	Error, in mg	Taken, in mg		S found, in mg	Error, in mg
S	Metal chloride, calculated in terms of oxide, 10.0			S	Metal chloride, calculated in terms of oxide, 10.0		
1,60	BaO	1,64	+0,04	3,20	NiO	3,19	−0,01
3,20	BaO	3,21	+0,01	1,60	CoO	1,61	+0,01
1,60	Fe_2O_3	1,54	0,06	3,20	CoO	3,14	−0,06
3,20	Fe_2O_3	3,19	−0,01	1,60	ZnO	1,65	+0,05
1,60	Al_2O_3	1,62	+0,02	3,20	ZnO	3,17	−0,03
3,20	Al_2O_3	3,16	−0,04	1,60	CdO	1,59	−0,01
1,60	Cr_2O_3	1,59	−0,01	3,20	CdO	3,17	−0,03
3,20	Cr_2O_3	3,15	−0,05	1,60	PbO	1,57	−0,03
1,60	MnO	1,64	+0,04	3,20	PbO	3,18	−0,02
3,20	MnO	3,18	−0,02	1,60	Bi_2O_3	1,65	+0,05
1,60	NiO	1,64	+0,04	3,20	Bi_2O_3	3,16	−0,04

In addition, sulfates were determined in sea-water. Using the classical gravimetric method, 0.00233 g of S was found in 5 ml of sea-water. Using the same volume of sea-water, and evaporating to dryness on a water bath, 0.00237 g of S was found by determination by the method involving reduction to H_2S.

Experimental Procedure. The most convenient amount of sample to take for analysis is that which contains about 0.5 − 5 mg of sulfate sulfur (calculated on the basis of S).

When the test material is a dry material, an aliquot of it is placed in the quartz holder and moistened with 2 − 3 ml of a 2% solution of potassium chloride and the mixture evaporated to dryness on a water bath.

When a solution is being analyzed, it is placed in a holder and potassium chloride added, when necessary, in the amount just quoted, and the whole evaporated to dryness.

When the test material contains nitrates, the dry residue in the holder is treated with concentrated hydrochloric acid and the mixture evaporated to dryness; this operation is repeated three times.

When very large amounts of chlorides are involved (more than 0.2 g), it is recommended that 3 − 4 drops of concentrated phosphoric acid be added to the dry residue, and the whole heated on a sand bath at 140 − 150 deg for 30 − 40 minutes for removing the bulk of the chlorides.

To test material prepared in any of the ways indicated, and contained in a holder is added 8 ml of reagent (to the mark on the holder), and, using a wire with a hook on it, the holder is transferred into the apparatus. The apparatus is sealed with a stopper filled with a tube for leading in CO_2, and with a thermometer. The absorption apparatus containing cadmium acetate is then connected and CO_2 passed for 3 − 5 minutes in order to drive the air from the apparatus. The apparatus is then heated over a small gas burner flame at such a rate that a temperature of 300 deg is reached in 15 − 20 minutes.

TABLE 3

Sample	S found, in %	
	By a gravimetric method	By reduction to H_2S
Gypsum	18,82	18,81
Grey slime	0,100	0,102
Black slime	0,066	0,067

Reduction starts at a temperature as low as 120 – 150 deg for high sulfate contents, the liquid in the holder becomes turbid as a result of deposition of elemental sulfur, the latter obviously being the intermediate form during reduction; on heating further, the sulfur is reduced to hydrogen sulfide and the liquid in the holder becomes clear.

At approximately 240 – 250 deg the reduction process starts to proceed vigorously as is evident from the bubbles of hydrogen sulfide liberated. When the temperature reaches 300 deg it is kept there for a further 25 – 30 minutes in order to complete the reduction. In order to check that reduction has gone to completion, the absorption tube can be disconnected and the gas issuing from it tested for hydrogen sulfide by means of lead acetate paper, or by its smell. When reduction is complete, the receiver containing cadmium sulfide is removed, and, using a piece of ashless filter paper, the sulfide adhering to the end of the tube wiped off; the contents of the receiver and the filter paper are shaken together and the whole added to acidified 0.02 N iodine solution. The flask is stoppered and then allowed to stand for 20 – 30 minutes, the contents being periodically shaken during this time; finally, excess iodine is titrated with 0.02 N thiosulfate.

1 ml of 0.02 N iodine corresponds to 0.00032 g S. For determining amounts of sulfur less than 0.5 mg, it is best to use 0.01 N iodine and thiosulfate.

SUMMARY

1. A study has been made of a method for determining sulfates by reducing them to hydrogen sulfide by means of a reagent prepared by evaporating divalent tin with concentrated orthophosphoric acid. Optimum conditions for preparing the reagent have been established.

2. A modified apparatus is described for carrying out the determination; rapid charging and prevention of corrosion of the apparatus by phosphoric acid are special features of the apparatus.

3. The method has been tried out on pure salts; it has been confirmed that calcium, barium, iron, aluminum, chromium, manganese, cobalt, nickel, and zinc do not interfere with sulfate determination. It has been established that the presence of the alkali metal chlorides in amounts up to 0.2 g accelerates the reduction process.

4. It has been established that bismuth, lead, and cadmium do not interfere with the reduction. It has been confirmed that copper and mercury salts interfere.

5. The method has been tried out on natural materials such as: gypsum, Black Sea silt, and sea water.

LITERATURE CITED

[1] V. Auger and M. Gabillon, Compt. rend., 152, 441 (1911).

[2] Lorant, Hoppe-Seyler, Z. physiol. Chem. 185, 245 (1929).

[3] H. Roth, Microchem. acta 36-37, 379 (1951).

[4] L. Pepkowitz and F. Shirle, Analyt. Chem. 23, 1709 (1951).

[5] O. Horak, Z. analyt. Chem. 139, 156 (1953).

[6] E. Archer, Analyst 81, 960, 181 (1956).

[7] E. Rancke-Madsen, Acta. Chem. scand. 3, 7, 773 (1949).

[8] T. Takagi, T. Kiba, I. Ioshimura and I. Kishi, Bull. Chem. Soc. Japan. 28, 9, 641 (1955).

[9] S. Ohashi, Bull. Chem. Soc. Japan 28, N 9, 645 (1955).

[10] T. Kiba, Bull. Chem. Soc. Japan. 30, N 1, 44 (1957).

[11] T. Kiba, I. Akaza and S. Taki, Bull. Chem. Soc. Japan. 30, N 5, 482 (1957).

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POLAROGRAPHIC DETERMINATIONS OF IODIDES IN MOLTEN SALTS

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Previous articles have dealt with the possibility of determining various anions in the anodic and cathodic regions in a supporting electrolyte consisting of molten nitrates (KNO_3 + $NaNO_3$) using the electrodes Pt_{micro} – Pt_{macro} [1]. It was established that a number of anions give stable waves in the cathodic and anodic regions. The behavior of chromates and nitrites in a supporting electrolyte of molten nitrates [2, 3] was studied in greater detail. The object of our further research was the I^- ion which gives well-defined waves in the anodic region.

The setup and the technique used have been described before [1 – 3].

Within the temperature range 270 – 390 deg, I^- ions give two well-defined waves on the polarograms in the anodic region. The first of these waves (the oxidation potential of which with respect to the platinum cathode is +0.8 – +0.6 volt) corresponds to anodic oxidation of iodide ions. The wave height depends on the concentration of iodide introduced; when the oxidation potential is reached, liberation of violet bubbles of gas on the electrode is observed for all temperatures. The second wave, which is absent in the supporting electrolyte of nitrates, and only appears when iodide is added to the melt, corresponds to the wave for NO_2^- ions is confirmed by the nearness of the oxidation potentials and half-wave of pure nitrite, and the second wave obtained. When the melt is acidified by addition of $KHSO_4$, the second wave disappears, while the first wave remains unaltered. The addition of an aliquot of $NaNO_2$ to the iodide melt increases the height of the second wave. Formation of NO_2^- in the melt after addition of KI can be explained by the occurrence of the reaction $2KI + KNO_3 \Leftrightarrow I_2 + KNO_2 + K_2O$. Potentiometric studies confirmed that this reaction does in fact occur.

TABLE 1

Reproducibility of Iodide Waves With Time

Temperature, in °C	Weight of KI, in mg	Wave height, in mm on the scale				
		Immediately	After 15 min.	After 30 min.	After 60 min.	After 120 min.
290±5	150,0	7,0	7,5	8.0		
		8,0	7,5	8,0		
		7,0	9,5	10.0	8,0	8,0
345±5	100,0	17,0	14.0	15.5	14.0	13.0
			16,0	18.0	14.5	14,5
			15.5	14.5	14.5	13.5
385±5	50,0	5,5	4,0	5,5	5,5	
		3,5	3,0	3,0	3,5	

Despite the interaction which occurs between KI and KNO_3, determination of I^- in a melt by a polarographic method is fully possible, as shown below. Obviously, some equilibrium state is established in the molten salts, and the iodide content can be determined polarographically.

The height of the first wave for I^- does not change during 30 – 120 minutes after addition of the aliquot of iodide, and exhibits fairly good reproducibility, as can be seen from the results given in Table 1.

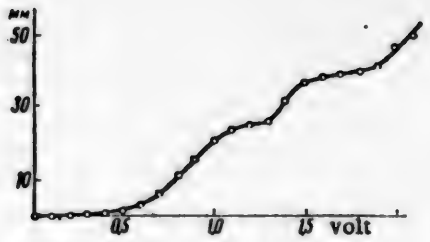

Fig. 1. Polarogram for the iodide ion.

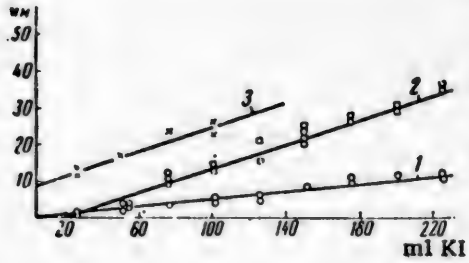

Fig. 2. Calibration curves for KI:
1) 280°; 2) 350°; 3) 390°.

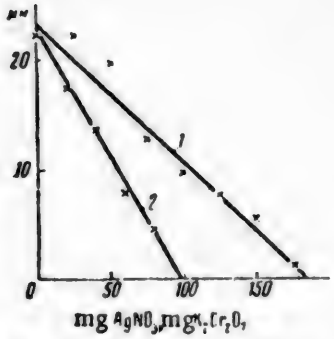

Fig. 3. Curve for amperometric titration:
1) 200 mg of KI with micro amounts of $AgNO_3$; 2) 200 mg of KI with micro amounts of $K_2Cr_2O_7$ at 280°.

The forward and reverse courses of the polarographic waves do not coincide. This is connected with changes which occur on the electrode during the polarographic process, particularly at elevated temperatures; these changes are manifested as blackening of the anode surface. In order to get reproducible results, it is necessary to clean the electrodes by calcining them.

During the determination of the half-wave potential with respect to the indifferent glass electrode, the graph for $E \log \frac{i}{i_d - i}$ proved to be a straight line. At 340 ± 5 deg, the half-wave potential is $E_{\frac{1}{2}} = 0.32 \pm 0.02$ volt, and is almost independent of the iodide concentrations.

In order to establish the behavior of the electrodes during the polarographic process, a study was made of changes in the electrode potentials during the polarographic process, with respect to a glass reference electrode, which was described in a previous article [3]. It was found that during the initial stages of the appearance of the polarographic wave, the anode potential changes only insignificantly while that of the cathode changes sharply. When the limiting current is reached, the anode potential changes sharply, while the cathode potential hardly changes at all.

In order to characterize the behavior of iodide ions, the temperature coefficient of the diffusion current was determined by two methods describe previously [3]. The temperature coefficient had a value of 1.5%/degree.

There is a linear relation between the value of the diffusion current and the iodide concentration of the melt (Fig. 2). Determination of various amounts of KI by means of a calibration curve gives completely satisfactory results (Table 2).

We were interested in the possibility of carrying out an amperometric titration of iodide ions in molten salts.

During titration of I^- with micro amounts of $AgNO_3$, a yellow insoluble precipitate of AgI is formed in the melt, and the height of the iodide wave gradually decreases. As can be seen from Fig. 3, the equivalence point, according to the amperometric curve, is fairly clear-cut. Titration gives satisfactory results (Table 3).

A systematic error on the side of low results for the amount of KI is always observed. This can be explained on the grounds that some of the KI, as mentioned already, reacts with the NO_3^- ions.

Titration of iodide ions with the oxidizing agent $K_2Cr_2O_7$ was carried out in both neutral and acid media. On addition of micro amounts of the oxidizing agent to a melt containing KI, the wave height for I^- gradually increases, giving a well-defined curve during amperometric titration (Fig. 3). Determination of the equivalence point is also fairly easy. Titration results are given in Table 4.

If it is assumed that the reaction $K_2Cr_2O_7 + 6KI \rightarrow 3I_2 + 2KCrO_2 + 3K_2O$, for which the molar ratio $K_2Cr_2O_7$/KI is equal to 0.166, takes place in the melt, then, as can be seen from Table 4, the amount of $K_2Cr_2O_7$ used up for titration is considerably greater. During potentiometric titration of dichromate with potassium iodide in a melt at the same temperatures, there is observed an increased expenditure of dichromate.

In Fig. 4 is shown the curve obtained during the potentiometric titration of 50 mg of $K_2Cr_2O_7$ with micro aliquots of KI in a neutral melt. As is evident from this Fig., the equivalence point lies at 96 mg, which corres-

TABLE 2

Determination of KI in a Molten Salt

Temperature, in °C	KI taken, in mg	KI found, in mg	Error, in %
280	116	114	−2
	200	180	−10
350	75	85	+13
	100	94	−6
380	25	29	+16
	100	80	−20

Mean experimental error ± 11%

TABLE 3

KI taken, in mg	$AgNO_3$ used, in mg	KI found, in mg	Error, in %
200	195	190.4	−5
176	180	170.0	−4
81	82	80.0	1.3

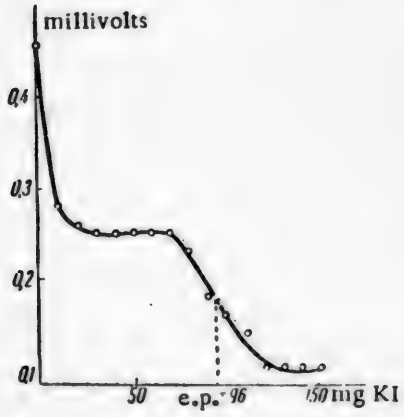

Fig. 4. Potentiometric titration curve for 50 mg of $K_2Cr_2O_7$ with micro amounts of KI.

ponds to a ratio of $K_2Cr_2O_7/KI = 0.3$, which is close to the value found polarographically. The molar ratio found corresponds more closely to the reaction $4K_2Cr_2O_7 + 12KI \rightarrow 8KCrO_2 + 12KIO \rightarrow 8KCrO_2 + 6K_2O + 6I_2 + 3O_2$. That this reaction does in fact occur should be proved by additional experiments or by other methods of investigation.

In one of the previous investigations on the polargraphy of cations in a supporting electrolyte of fused nitrates [4], the process of complex formation between cadmium and iodide ions was detected polarographically. The existence of this reaction was also confirmed in the present investigation, and an attempt was made to use it for amperometric titration of iodide ions in the melt.

On addition to a molten salt (temperature 290°), containing iodide atoms, of micro aliquots of cadmium nitrate, the iodide wave disappeared and a new wave appeared at a more negative potential, namely at 0.3 − 0.4 volt relative to the platinum cathode. The addition of cadmium iodide instead of potassium iodide gave a wave at a potential of 0.3 − 0.4 volt. The height of this wave is proportional to CdI_2 concentration, but its height is approximately half of that of the wave obtained for an equimolecular concentration of $K_2[CdI_4]$. Obviously complex formation of $2CdI_2 \rightarrow Cd[CdI_4]$ occurs in the melt.

TABLE 4

Titration of KI with Micro Amounts of $K_2Cr_2O_7$

Temperature, in °C	Medium	Ki taken, in moles	$K_2Cr_2O_7$ used, in moles	Molar ratio $/K_2Cr_2O_7/$ /KI/
280	Neutral	$1,2 \cdot 10^{-3}$	$0,34 \cdot 10^{-3}$	0,28
	»	$1,2 \cdot 10^{-3}$	$0,30 \cdot 10^{-3}$	0,25
	Acid	$1,2 \cdot 10^{-3}$	$0,54 \cdot 10^{-3}$	0,45
	»	$1,2 \cdot 10^{-3}$	$0,37 \cdot 10^{-3}$	0,41
350	Neutral	$1,2 \cdot 10^{-3}$	$0,29 \cdot 10^{-3}$	0,24
	»	$1,2 \cdot 10^{-3}$	$0,36 \cdot 10^{-3}$	0,30
	»	$0,9 \cdot 10^{-3}$	$0,32 \cdot 10^{-3}$	0,36

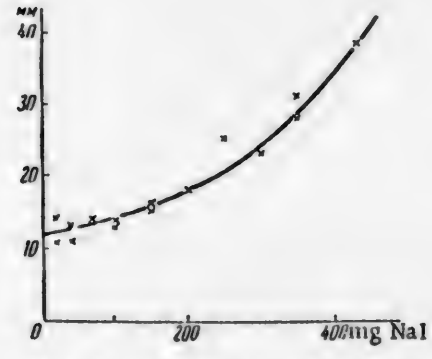

Fig. 5. Calibration curve for NaI.

In order to make sure that the waves indicated do in fact belong to the complex $[CdI_4]^{2-}$, the complex $K_2[CdI_4]$ was synthesized in the solid state and added to a melt. The same clearly defined wave was again detected on the polarogram at 0.3 volt. There was found to be a linear relation between the concentration of the complex and the wave height.

The analogous iodide complex of lead is apparently unstable. Attempts to use the process of complex formation for determination of iodide ions in melts did not give good results.

We thought it would be of interest to clarify the behavior of iodide ions in a supporting electrolyte of fused chlorides. The supporting electrolyte tried was a mixture of equal parts of potassium, sodium, and lithium chlorides. The work was carried out at a temperature of 700 – 750 deg. On addition of sodium iodide to the fused chlorides, fairly clearly defined waves were obtained in the anodic region, almost from zero applied potential. The relation between wave height and concentration of sodium iodide is a complex one (Fig. 5).

N. Zotova and E. Levinzon, who are students at the Kishinev University, took part in the work described here.

SUMMARY

It has been shown that it is possible to determine I^- polarographically in a supporting electrolyte of fused nitrates at temperatures of 270 – 390 deg, and in fused chlorides at temperatures of 700 – 750 deg. It has been established that there is a linear relation between the concentration of iodide ions in the melts and the height of the polarographic wave when fused nitrates are used as the supporting electrolyte. The half-wave potentials of I^- in fused nitrates have been determined. It has been shown that it is possible to carry out amperometric titration of I^- with micro aliquots of silver nitrate and potassium dichromate.

The occurrence of complex formation between I^-, Cd^{2+}, and Pb^{2+} in fused nitrates has been confirmed.

LITERATURE CITED

[1] Iu. S. Lialikov, R. M. Novik and D. M. Palade, Theses of Reports of the Scientific Conference of the Kishinev University, Kishinev, p. 66 (1955) [in Russian].

[2] Iu. S. Lialikov and V. A. Kovalenko, Sci. Trans. Kishinev University, 14, p. 137 (1954).*

[3] Iu. S. Lialikov and R. M. Novik, Sci. Trans. Kishinev University, 26, p. 61 (1957).*

[4] Iu. S. Lialikov, Factory Labs. 17, 909 (1951).

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* In Russian.

RAPID METHODS OF MICROELEMENTAL ANALYSIS

COMMUNICATION 15. THE SIMULTANEOUS MICRO DETERMINATION OF CARBON, HYDROGEN, AND HALOGENS IN ORGANIC COMPOUNDS*

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In previous articles we have described methods for the simultaneous micro determination of carbon, hydrogen, and halogens by pyrolytic combustion in an empty tube [1 – 2], and also described apparatus which we have innovated [3]; in addition, the characteristics of the elemental analysis of halogen-containing materials have been considered [4]. It was established that the presence of halogens, or of halogen-containing materials, exhibits an inhibiting action on the oxidation of carbon to carbon dioxide, as a result of which, the gases issuing from the combustion tube have been found to contain carbon monoxide. In order to ensure quantitative oxidation of carbon to CO_2 during the analysis of halogen-containing compounds, it was found necessary to introduce platinum contacts into the oxidizing zone. At the same time it was shown that, in those cases where absorption of the halogen was carried out immediately after the products of pyrolytic combustion had left the quartz test tube, and the gases freed from halogen passed into the oxidizing zone, quantitative conversion of carbon into CO_2 could be achieved without using a platinum catalyst. Nevertheless, as pointed out already [4], such an experimental technique would preclude simultaneous determination of C, H, and halogen.

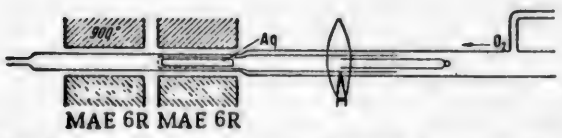

Fig. 1. Apparatus for the simultaneous determination of carbon, hydrogen, and halogens.

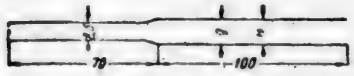

Fig. 2. "Case" 8.5 and 11 mm external diameter; 9 mm internal diameter.

Recently a technique has been developed in our laboratory, in which, by carrying out the combustion in a so called "case" [5], it has been found possible to introduce essential improvements into the determination of carbon, hydrogen, and halogens. In this new variant, the tube containing the sample, silver, and the oxidizing zone are arranged successively in the gas flow in the combustion tube. For this purpose the silver and the tube containing the sample are placed in a hollow thin-walled quartz "case" (Fig. 2), which, after combustion, is removed from the tube and weighed. In this case, as mentioned already [4], there is no need to place platinum contacts in the oxidizing zone, but, at the same time it is possible to weigh the silver by using the "case". The weight of the "case" is almost half that of the apparatus used previously, which included a heavy ground joint; accordingly, it is possible to achieve considerably better reproducibility in weighing the silver, and, thereby, essentially improve the accuracy of halogen determination. In addition, there is no further need to use a combustion tube with ground joints, and the life of the tube itself is increased (Fig. 3), since it is not corroded by the silver which is located in the "case".

*For Communication 14, see J. Anal. Chem. 12, 526 (1957).

The halogens are absorbed by pure metallic silver in the form of foil, mesh, or wire,* or by silver precipitated on a carrier. When metallic silver is used in the "case" about 1.5 g is introduced into the "case"; this is approximately half the amount used in the ground-joint absorption apparatus [4]. The layer of silver 5 – 6 cm long is heated with the MAG-6R electric oven to 550 – 600 deg. This amount of silver can be used for 30 – 40 determinations; this corresponds to an increase in weight as a result of absorption of halogen of about 70 mg. Table 1 contains results for the absorptive capacity of metallic silver expressed in milligrams of halogen per g of silver. Comparison of our results with those of Mitsui [6], which he obtained during a detailed study of the determination of halogens in organic compounds, confirm a conclusion which we had already come to previously, that the absorptive capacity of metallic silver depends not only on its surface area, but also on the temperature [4]. In the case under discussion, increasing the temperature from 425 – 575 deg led to the absorptive capacity increasing several times.

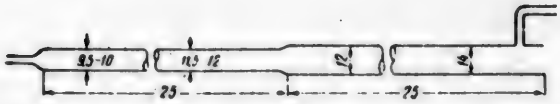

Fig. 3. Combustion tube. 9.5 – 10 mm and 12 mm internal diameter; 11.5 – 12 mm and 14 mm external diameter.

Our experiments also confirmed results obtained by Mitsui which showed that silver preparations with a large surface area have a good absorptive capacity at temperatures which are too low for use with silver mesh or foil. Of particular interest in this connection is a preparation of silvered pumice, since, according to our observations, silver deposited on a porous carrier absorbs halogen very well, and corrodes the walls of the quartz tube to a considerably lesser extent than metallic silver. This is a consequence of the fact that the main bulk of the silver halide is held by the well-developed surface and does not fall on the quartz walls. For the simultaneous determination of C, H, and halogen, we tried granulated, silvered pumice prepared according to Sokolova's method [7], and became convinced of its completely suitability for our purpose. The silvered pumice was tested at 425 deg, i.e. at a temperature which is lower than the melting point of the silver halide, which is 455, 434, and 588 deg for AgCl, AgBr, and AgI, respectively. In the course of these tests it established that the absorptive capacity of this preparation was almost double that of the electrolytic silver proposed by Mitsui (Table 2).

TABLE 1

Absorptive Capacity of Metallic Silver at 575 deg

Weight of silver, in g	Number of determinations carried out with same aliquot of silver	Amount of halogen trapped by the silver in mg	Absorptive capacity of silver for halogen, in mg of halogen per g	Weight of silver, in g	Number of determinations carried out with same aliquot of silver	Amount of halogen trapped by the silver in mg	Absorptive capacity of silver for halogen, in mg of halogen per g
1,45	42	88	61	1,36	40	81	60
1,18	32	77	65	1,62	32	65	40
1,18	25	76	64				
0,80	18	47	59	Mean 1,27		72	58

In addition to more complete use of the silver, another advantage of working with such a preparation is that, thanks to absorption of the halogen at a comparatively low temperature (425 – 575 deg), corrosion of the case is so insignificant, that the latter can be used repeatedly with fresh lots of preparation.

When metallic silver is used, the silver halide spills over the "case", which, as a rule, comes out of the stream after the first series of experiments.

The silvered pumice should not completely fill the cross section of the "case", since, if this is done, there will be some resistance to the gas flow, which will be sufficient to direct part of the gaseous combustion products into bypassing the pumice layer.

* We had at our disposal silver foil 0.04 mm thick, and mesh made from 0.1 mm diameter wire.

TABLE 2

Absorptive Capacity of Various Silver Preparations

	Metallic silver in the form of mesh, foil, or wire		Electrolytic silver	Silvered pumice
	Mitsui's results	Author's results	Mitsui's results	Author's results
Temperature at which the silver is heated	425°	575°	425°	425°
Absorptive capacity expressed in mg halogen per g of silver	3.7	55	162	292

TABLE 3

Determination of Carbon and Chlorine in Hexachloroethane

Test material	C, in %		Cl, in %		Total C and Cl, in %	Notes
	found	difference	found	difference		
Hexachloroethane C_2Cl_6	7.68	−2.46	82.85	−6.99	90.53	Combustion carried out with a gas burner
	9.59	−0.55	85.72	−4.14	95.31	
C—10.14%	10.25	+0.11	89.66	−0.20	99.91	Combustion carried out with an electric oven
Cl—89.86%	10.22	+0.08	89.59	−0.27	99.81	

Experimental Procedure. Before commencing an analysis, a blank is carried out while the ovens are on. For this purpose, the "case" containing the silver is moved into the combustion tube, and the oven fitted onto the part where the silver is located; when metallic silver is used, the oven temperature is raised to 575 deg, while when silvered pumice is used the temperature is adjusted to 425 deg. The absorption apparatus is connected to the combustion tube and 500 ml of oxygen passed through at a rate of 35 − 40 ml/minute. When the blank test is finished, the absorption apparatus is disconnected, and, after wiping it and removing the electric charge on it, it is transferred to the balance. The electric oven is removed from the "case" and the latter is then cooled in a weak oxygen stream in the course of 7 − 8 minutes. The "case" is removed from the combustion tube by means of a hook, and is then electrically discharged by passing it over the oxidizing flame of a burner, and placed on a long block near the balance. The absorption apparatus is weighed 15 and 20 minutes after wiping. After weighing the absorption apparatus, the "case" is weighed 25 minutes after wiping the apparatus. The weighed apparatus is connected to the setup and left under oxygen pressure with the aspirator tap closed. An aliquot of test material is weighed into a tube and the latter placed in the "case", the whole is then placed in the combustion tube. The tube containing the sample is placed approximately halfway along the "case". In some cases the analyst may find it more convenient to use a tube 9 cm long; the latter is placed at a position $\frac{1}{5}$ the length of the "case". Long tubes are used for pyrolysis of readily volatile compounds (b.p. 40 − 50 deg) and organosilicon compounds which contain halogens. Combustion of fully halogenated hydrocarbons is best carried out with a MAG-6R electric oven at 900 deg rather than with a gas burner. Table 3 contains some comparative results which show that analysis of hexachloroethane by means of a gas burner leads to incomplete combustion. Results of analysis of halogen-containing materials carried out by the technique just described are given in Table 4.

The same operational procedure and apparatus can also be used for the simultaneous determination of C, H, and S, the only difference in this case is that the silvered pumice is kept at a temperature of 750 deg. It is

TABLE 4

Simultaneous Determination of Carbon, Hydrogen, and Halogen

Test material	Amount of sample taken, in mg	C, in %		H, in %		Halogen, in %	
		found	difference	found	difference	found	difference
1, 1, 1,2-Tetrachloro-3-p-tolylpropane	6,558	44,16	+0,01	3,78	+0,07	52,20	+0,06
$C_{10}H_{10}Cl_4$	6,884	44,14	−0,01	3,80	20,09	52,22	+0,08
C—44, 15%; H-3,71%; Cl-52, 14%							
Hexachloroethane	8.145	10,22	+0,08	—	—	89,53	−0,33
C_2Cl_6	9.900	10.30	+0,16	—	—	89,71	−0,15
C—10, 14%; Cl – 89, 86%							
p-Chlorosuccinic acid	7,444	59,13	−0,06	3,78	−0,08	19 21	−0,21
$C_4H_5ClO_2$	9,767	59,09	−0,10	3,94	+0,08	19,25	−0,17
C—59, 19%; H—3, 86%; Cl—19, 42%							
Bromobenzoic acid	6,015	42,01	+0,19	2,61	+0,10	39.87	+0,12
$C_7H_5BrO_2$	6,880	41,95	+0,13	2,66	+0,15	39,61	−0,14
C—41, 82%; H—2, 51%; Br-39, 75%							
α, β-Dibromoethyl-2-propoxybenzene	8,387	41,28	+0,17	4,50	+0,12	49,74	+0,11
$C_{11}H_{14}Br_2O$	6,112	41,10	+0,09	4,49	+0,11	49,49	−0,14
C—41, 01%; H—4, 38%; Br-49, 63%							
Acetovinyltrimethyl-ammonium chloride	6,615	51,27	−0,10	8,64	+0,02	21.87	+0,20
$C_7H_{14}ClNO$	8,050	51,30	−0,07	8,66	+0,04	21,64	−0,03
C—51, 37%: H—8, 62%; Cl – 21, 67%							
Triphenyloxonium iodide	6,960	57,91	+0,14	4,03	−0,01	34,31	+0,39
$C_{18}H_{15}IO$	7,778	57,99	+0,22	4,03	−0,01	34,07	+0,15
C—57, 77%; H—4, 04%; I—33, 92%							
2-Phenyldihydroquinolizine perchlorate	6,526	59.00	+0,07	4,04	+0,08	11,55	−0,05
$C_{15}H_{12}ClNO_4$	6,410	59,07	+0,14	4,07	+0,11	11,73	+0 13
C-58. 93%; H—3,96%; Cl—11, 60%							

necessary to use different "cases" for the determination of sulfur and halogens. Results for the determination of C, H, and S are given in Table 5.

As is evident from the results given in Tables 5, 6, and 7, in those cases where the test material contains halogen or sulfur, the technique involving the use of a "case" is applicable to methods developed earlier for the simultaneous determination of several elements on one aliquot of test material, namely, to the determination of carbon, hydrogen, halogen, and silicon [8 – 11], carbon, hydrogen, sulfur, and phosphorus [12 – 14], carbon, hydrogen, halogen, or sulfur and metal [4]; the latter is possible only when, as the result of combustion, nonvolatile metal oxides or salts which are stable at a temperature of 900 deg are obtained. Determinations which we have carried out of carbon, hydrogen, halogen, and inorganic residue on one aliquot of test material which contained in addition to C, H, and I, one atom each of phosphorus and copper, showed that under the conditions of pyrolytic combustion, the weight of inorganic residue corresponds to copper pyrophosphate, and that it is possible on the basis of this residue to calculate the content of copper and phosphorus in materials of a similar type (Table 7). The results given in Tables 4, 5, 6, and 7 illustrate the possibilities which are opened up by the use of pyrolytic combustion during the analysis of organic compounds with a complex composition.

TABLE 5

Simultaneous Determination of Carbon, Hydrogen, Sulfur, and Some Other Elements

Test material	Amount of sample taken, in mg	C, in %		H, in %		S, in %		P, in %		Fe,* in %	
		found	difference	found	difference	found	difference	found	difference	found	difference
Sulfanilic acid	8.741	41,84	+0,23	4,21	+0,14	18.51	−0				
$C_6H_7NO_3S$	7.700	41,61	0	4,22	+0,15	18,47	−0,04				
C−41,61%; H−4,07%; S−18,51%											
Phenylsemicarbazone of 0,0-diethyl-S-acetonyldithiophosphate	6,790	58,25	−0,10	8,02	−0,14	8,65	0				
$C_{16}H_{30}N_2O_4S$	5,848	58,29	−0,06	8,01	−0,15	8,69	+0,04				
C−58,35%; H−8,16%; S−8,65%											
Phenylsemicarbazone of 0,0-diethyl-S-acetonyldithiophosphate	5,578	44,82	+0,04	5,73	−0,18	17,14	+0,06	8,19	−0,06		
$C_{14}H_{22}N_3O_3PS_2$	5,761	45,00	+0,22	6,01	+0,10	17,06	−0,02	8,19	−0,06		
C−44,78%; H−5,91%; S−17,08%; P−8,25%											
Ferrocenylthiocyanomethane	7,045	55,95	−0,10	4,32	+0 01	12.18	−0,29	—	—	21,88	+0,16
$C_{12}H_{11}FeNS$	5,682	55,87	−0,18	4,45	+0,14	12,02	−0,45	—	—	21,54	−0,18
C−56,05%; H−4,31%; S−12,47%; Fe−21,72%											

* Calculated from the weight of Fe_2O_3

TABLE 6

Simultaneous Determination of Carbon, Hydrogen, Chlorine, and Silicon

Test material	Amount of sample taken, in mg	C, in %		H, in %		Cl, in %		Si, in %	
		found	difference	found	difference	found	difference	found	difference
Methyldodecyldichlorosilane	5 890	55,32	+0,21	9,93	+0,03	24,70	−0,33	9,57	−0,33
$C_{13}H_{28}Cl_2Si$	5,670	55,28	+0,17	9,90	−0,06	25,22	+0,19	9,80	−0,10
C−55,11%; H−9,96%; Cl−25,03%; Si−9, 90%									
Decyltrichlorosilane	7.725	43.68	+0,12	7,79	+0,11	38,21	−0,37	10,58	+0,40
$C_{10}H_{21}Cl_3Si$	5,802	43,71	+0,15	7,71	+0,03	38,03	−0,55	10,55	+0,37
C−43,56%; H−7,68%; Cl−38,58%; Si−10,18%									

TABLE 7

Simultaneous Determination of Carbon, Hydrogen, Iodide, and Inorganic Residue

Test material	Amount of sample taken, in mg	C, in %		H, in %		I, in %		Cu, in %		P, in %*	
		found	difference	found	difference	found	difference	found	difference	found	difference
Complex formed between copper iodide and dipropyl phosphinate	7,718	34,47	−0,12	4,65	+0,05	30,77	+0,31	15 35	+0,10	7,49	+0,05
$C_{12}H_{10}CuIO_2P$	7.296	34,58	−0,01	4,73	+0.13	30,25	−0,21	15,36	+0,11	7,49	+0,05
C−34,59%; H−4,60%; I−30,46%; Cu−15,25%; P−7,44%;											
Complex formed between copper iodide and diethyl phenylphosphinate	7,720	30,81	−0,09	3,91	+0,02	33,08	+0,42	16,35	—	7,97	—
$C_{16}H_{15}CuIO_2P$	6,130	30,55	−0,35	3,83	−0,06	33,25	+0,59	16,18	−0,17	7,89	−0,08
C−30,90%; H−3,89%; I−32,66%; Cu−16,35%P−7,97%											

* Calculated on the basis of a residue of $Cu_2P_2O_7$.

SUMMARY

An improved modification of the method for the simultaneous determination of C, H, and halogen has been developed. Thanks to the use of a "case", the accuracy of determination of the halogen is high, and there is no need to use platinum contacts, while a combustion tube of the normal type without any ground-glass joints can be used.

Silvered pumice is used for absorbing the halogens, and it has been demonstrated that this material can be used at 425 deg; it has been shown that at this temperature the absorptive capacity of silver precipitated on pumice is considerably greater than that of electrolytic silver.

The method described is also applicable to the determination of C, H, and S, and for the determination of several elements on one aliquot of test material, in accordance with methods developed previously.

LITERATURE CITED

[1] M. O. Korshun and N. S. Sheveleva, Proc. Acad. Sci. 60, 63 (1948).

[2] M. O. Korshun and N. E. Gel'man, "New Methods of Elemental Micro Analysis," Moscow, (1949).*

[3] M. O. Korshun and N. S. Sheveleva, J. Anal. Chem. 7, 104 (1952).**

[4] M. O. Korshun and N. S. Sheveleva, J. Anal. Chem. 11, 376 (1956).**

[5] N. E. Gel'man, M. O. Korshun, and N. S. Sheveleva, J. Anal. Chem. 12, 526 (1957).**

[6] T. Mitsui and H. Sato, Microchimica acta, No. 11, 1603 (1956).

[7] N. V. Sokolova, J. Anal. Chem. 11, 728 (1956).**

[8] V. A. Klimova, M. O. Korshun and E. G. Bereznitskaia, Proc. Acad. Sci. 84, 1175 (1952).

[9] V. A. Klimova, M. O. Korshun and E. G. Bereznitskaia, Proc. Acad. Sci. 96, 81 (1954).

[10] V. A. Klimova and E. G. Bereznitskaia, J. Anal. Chem. 9, 223 (1956).**

[11] V. A. Klimova and E. G. Bereznitskaia, J. Anal. Chem. 11, 292 (1956).**

[12] V. A. Klimova, M. O. Korshun and E. G. Bereznitskaia, Proc. Acad. Sci. 96, 287 (1954).

[13] M. O. Korshun, E. A. Terent'eva and V. A. Klimova, J. Anal. Chem. 9, 275 (1954).**

[14] M. O. Korshun, E. A. Terent'eva and V. A. Klimova, Proc. Acad. Sci. 100, 707 (1955).

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A METHOD FOR THE QUANTITATIVE DETERMINATION OF HALOGENS IN ORGANIC MATERIALS

COMMUNICATION 3. SIMULTANEOUS, INDEPENDENT, GRAVIMETRIC DETERMINATION OF CHLORINE, BROMINE, AND IODINE TAKEN TWO AND THREE ELEMENTS AT A TIME*

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In our first two communications we described new methods for the quantitative determination of chlorine, bromine, and iodine in organic materials [1]. The present article is devoted to the quantitative determination of the halogens, taken two and three elements at a time, on one aliquot of test material. Some of the methods for the simultaneous quantitative determination of halogens are long and complicated to carry out [2]. The principle of our method is based on displacement of the less active halogens from potassium and sodium bromides and from potassium iodide by the more active halogens.

At room temperature, the reaction of mutual liberation which occurs between the halogens does not occur in the absence of water. As we found out, on raising the temperature, the capacity of the halogens to liberate one another from their compounds with metals rapidly increases; the reaction is quantitative at temperatures of 680 – 720 deg for sodium and potassium bromides, and at 480 – 520 deg for potassium iodide.

The temperature should not be taken over those indicated above, since, in the case of the bromides, they fuse, while the iodides start to decompose appreciably.

The apparatus is assembled as shown in the diagram.

The first oven is heated to 750 – 800° deg, the second to 800 – 900° deg, the third to 680 – 720° deg, and the fourth to 480 – 520° deg.

The temperature of ovens 3 and 4 is measured by thermocouples. The temperatures are controlled within the limits indicated by means of laboratory autotransformers. Absorbing tube b is filled with sodium or potassium bromide, and tube c with potassium iodide. In order to prevent the absorbent from emptying out of the tubes, the openings of the tube are sealed with glass wool. About 30 – 35 g of chemically pure potassium bromide or iodide is usually used for filling one absorption tube.

One filling is sufficient for carrying out 30 – 50 determinations when the weight of the aliquot taken is 0.1 – 0.05 g.

The absorption tubes, which are made from quartz or high-melting glass, are interconnected by means of rubber tubing.

Purified and dried oxygen is passed for 30 – 35 minutes at the rate of 150 – 250 ml/minute through the assembled apparatus, the ovens of which are heated to the respective temperatures indicated above. It is essential to make sure that the oxygen flow is free and uniform.

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*For Communication 2, see J. Anal. Chem. 13, 595 (1958).

When sufficient oxygen has been passed through the apparatus, tubes b and c are disconnected and sealed with rubber tubes and transferred to the balance room; after standing for 30 – 40 minutes they are weighed without the rubber tubes, and closely fitting smoothed glass rods are inserted into the tubes instead of the rubber tubing, in order to decrease diffusion of oxygen.

Experimental Procedure. The tared absorption tubes are connected into the system. While they are being heated to the requisite temperature (5 – 10 minutes), the gasometer is filled with oxygen. 2 – 3 g of potassium iodide is introduced into the moist tube d, care being taken that the layer of potassium iodide is not too moist and compact, in order to avoid limiting the oxygen throughput.

5 – 8 ml of a 10% solution of potassium iodide is poured into the Winkler apparatus. The test material is weighed in a boat and is sprinkled with powdered quartz sand or chromic oxide, and is then inserted into the combustion tube a so that it is located at a distance of 2 – 3 cm from the origin of the first oven; the sample is then ignited by gradually moving 1 forward. Oxygen is passed through the apparatus at a rate of 150 – 250 ml/minute. Combustion takes 10 – 30 minutes, depending on the nature of the test material. When combustion is complete, tube a is calcined all along its length for 5 – 10 minutes; the oxygen is switched off and the absorption apparatus disconnected. Tubes b and c are transferred to the balance room and then weighed as indicated above.

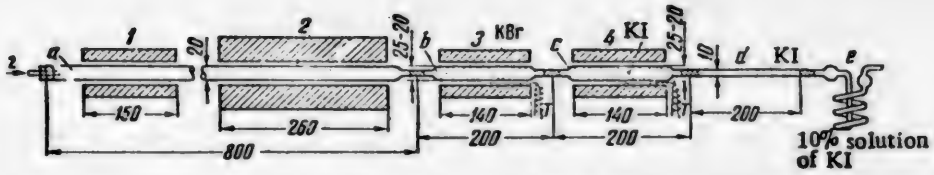

Fig. a) Quartz tube; b and c) absorption tubes; 1, 2, 3, 4) electric ovens; T) thermocouple; d) tube containing moist potassium iodide; e) Winkler apparatus containing 10% potassium iodide solution.

The contents of tube d and the Winkler apparatus are transferred quantitatively to a flask and the iodine titrated with 0.05 N sodium thiosulfate.

Calculation of the percentage chlorine and bromine is based on the changes in weight of tubes b and c, while the percentage of iodine is calculated on the basis of the results obtained on titrating the iodine liberated, and then condensed in tube d and apparatus e, with sodium thiosulfate.

Calculation of the Percentage Content of Chlorine, Bromine, and Iodine

1. Test Material Contains Chlorine and Bromine.

Calculations are based on the formulas:

$$\%\ \mathrm{Cl} = \frac{\mathrm{Cl}\cdot b_1\cdot 100}{(\mathrm{Br}-\mathrm{Cl})\,A} = 79{,}752\,\frac{b_1}{A}. \qquad (\mathrm{I})$$

$$\%\ \mathrm{Br} = \frac{\mathrm{Br}\cdot b_2\cdot 100}{(\mathrm{I}-\mathrm{Br})\cdot A} - \frac{\mathrm{Br}\cdot b_1\cdot 100}{(\mathrm{Br}-\mathrm{Cl})\cdot A} = \frac{170{,}02\cdot b_2 - 179{,}75\cdot b_1}{A} \qquad (\mathrm{II})$$

The correctness of the results obtained can be controlled on the basis of the iodine liberated, and subsequently absorbed in tube d and apparatus e.

The amount of iodine titrated should be equivalent to the sum of the chlorine and bromine.

2. Test Material Contains Chlorine and Iodine

The percentage content of chlorine is calculated by means of formula (I), while that of iodine is calculated by means of formula (III)

$$\%\,I = \frac{I \cdot K \cdot N \cdot 100}{A \cdot 1000} - \frac{I \cdot b_1 \cdot 100}{(Br - Cl)\,A} = \frac{12{,}692 \cdot K \cdot N - 285{,}47 \cdot b_1}{A}. \qquad \text{(III)}$$

3. Test Material Contains Bromine and Iodine

The percentage content of bromine is calculated by means of formula (IV), while that of iodine is calculated by means of formula (V)

$$\%\,Br = \frac{Br \cdot 100 \cdot b_2}{(I - Br) \cdot A} = 170{,}02 \cdot \frac{b_2}{A} \qquad \text{(IV)}$$

$$\%\,I = \frac{I \cdot K \cdot N \cdot 100}{1000 \cdot A} - \frac{I \cdot 100 \cdot b^2}{(I - Br) \cdot A} = \frac{12{,}692 \cdot K \cdot N - 270{,}02 \cdot b_2}{A}. \qquad \text{(V)}$$

4. Test Material Contains Chlorine, Bromine, and Iodine.

When the test material contains all three halogens, the chlorine content is calculated by means of formula (I), that of bromine by means of formula (II), and that of iodine by means of formula (V).

TABLE

Test material	% Chlorine			% Bromine			% Iodine		
	calculated	found	difference	calculated	found	difference	calculated	found	difference
1) p-Dichlorobenzene Dibromosuccinic acid	25,75	25,61	−0,14	26,99	26,88	−0,11			
2 p-Dichlorobenzene Dibromosuccinic acid	24,36	24,26	−0,10	28,67	28,72	+0,05			
3) p-Dichlorobenzene Hexabromoethane	23,15	23,09	−0,06	49,52	49,46	−0,06			
4) p-Dichlorobenzene Hexabromoethane	25,54	25,49	−0,05	44,82	45,03	+0,21			
5) p-Dichlorobenzene Iodoform	29,51	29,43	−0,08	—	—	—	37,51	37,50	−0,01
6) 2,4-Dichlorophenoxybutyric acid Iodoform	16,64	16,52	−0 12	—	—	—	40,17	40,11	−0,06
7) Monochloroacetic acid Iodoform	21,19	21,17	−0,02	—	—	—	42,27	42,22	−0,05
8) Dibromosuccinic acid Iodoform	—	—	—	57,93	57,72	−0,21	47,78	47,57	−0,21
9) p-Dibromobenzene Iodoform	—	—	—	67,76	67,62	−0,14	55,33	55,21	−0,12
10)p-Dichlorobenzene p-Dibromobenzene Iodoform	19,99	20,06	+0,07	23,74	23,67	−0,07	22,75	22,73	−0,02
11) Monochloroacetic acid Tetrabromoorthoxylene Iodoform	13,28	13,21	−0,07	21,60	21,52	−0,08	34,87	34,79	−0,08
12) p-Dichlorobenzene Dibromosuccinic acid Iodoform	20,39	20,19	−0,20	18,35	18,34	−0,01	25,18	25,11	−0,07

Arbitrary Designations in the Formulas: Cl is the gram-equivalent of chlorine; Br is the gram-equivalent of bromine; I is the gram-equivalent of iodine; A is the weight of test material.

K is the number of mls of thiosulfate used for titrating the iodine; N is the normality of the sodium thiosulfate solution.

b_1 is the change in weight of the tube containing sodium or potassium bromide; b_2 is the change in weight of the tube containing potassium iodide.

Results obtained by this method are contained in the Table.

SUMMARY

A new gravimetric method is described for the determination of halogens in organic materials.

The method is based on the mutual displacement of the halogens by one another from metallic bromides and iodides on heating.

In order to get quantitative results it is necessary to heat potassium and sodium bromide to 680 – 720 deg, while potassium iodide has to be heated to 480 – 520 deg.

The new method is fairly simple, reliable, rapid, and accurate, and does not require expensive and complicated apparatus.

The error for quantitative determinations is within 0.1 – 0.2%.

A single analysis takes 50 – 60 minutes.

LITERATURE CITED

[1] P. N. Fedoseev and M. Ia. Sobko, J. Anal. Chem. 10, 323 (1955).*

[2] G. Maier, "Analysis and Determination of the Structure of Organic Materials," Kharkov – Kiev, p. 153-155 (1935).**

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DETERMINATION OF THE CONCENTRATION OF TERTIARY BUTANOL AND ACETONE IN THE OXIDATION PRODUCTS OF ISOBUTANE, BY MEANS OF THEIR INFRARED ABSORPTION SPECTRA

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In studying the kinetics of chemical reactions it is very important to be able to carry out accurate, rapid, and simple determinations of the reaction products present in small amounts of test sample. In such cases it is often expedient to use infrared spectroscopy. Apart from functional analysis which is based on characteristic absorption bands, e.g. bands characteristic of vibrations of the C=O bond, and of alcoholic OH, etc., it is often possible to determine individual materials.

We came up against considerable difficulties in trying to apply chemical methods to the determination of the concentration of acetone and tertiary butanol in the oxidation products of isobutane in the presence of hydrogen bromide. Accordingly, we used the absorption spectra of these compounds in the infrared for analytical purposes.

There are published references [1] to the determination of these products during a study of the breakdown of ditertiary butyl peroxide, on the basis of the characteristic absorption band of the ketone at 5.98 μ, of the alcohol band at 2.925 μ, and of the peroxide band at 11.46 μ. For this purpose, however, it is necessary to change the spectrometer prism: for the bands at 5.88 and 11.46 μ a NaCl prism is used, while for the band of the alcoholic OH group at 2.92 μ, the prism used is a LiF one. In addition, in the latter instance, in order to avoid distortion of the results because of intermolecular interactions, high dilutions are used, and, accordingly large cell thicknesses.

All this means that the cells have to be filled more than once, and one simply cannot register the appropriate parts of the spectrum without additional manipulations and a considerable expenditure of test material.

Comparison of the absorption spectra of solutions of the main oxidation products of isobutane — tertiary butyl peroxide, tertiary butanol, and acetone — in CCl_4, in the region 1700 — 800 cm^{-1}, showed the presence of bands suitable for analytical use (Fig. 1).

The absorption bands of acetone and the peroxide do not overlap the absorption band of the alcohol at 918 cm^{-1}. The band at 1718 cm^{-1} which is characteristic of the C=O bond is convenient for determination of acetone [2]. The use of CCl_4 as a solvent means that it is possible to reduce the operation of determining these compounds, on the basis of the bands indicated, to registering the spectra for only one filling of a cell 0.3 mm thick. The optical density D is found from the spectrogram [3], while the molar concentration C is calculated from the Lambert-Beer relation:

$$D = KCl$$

where l is the cell thickness in cm; K is the absorption coefficient $mol^{-1}\ l/cm^{-1}$ ("apparent" [4] absorption coefficients without apparatus corrections are adduced). The absorption coefficient of the absorption band at 1718 cm^{-1} for acetone, is K = 300 $mole^{-1}\ l/cm^{-1}$ for a spectral slit width of 12 cm^{-1}. The absorption coefficient of the band for tertiary butanol at 918 cm^{-1} is K = 90 $mole^{-1}\ l/cm^{-1}$ for a spectral slit width of 6 cm^{-1}.

Fig. 1. Spectra of tertiary butanol, acetone, and tertiary butyl peroxide in CCl_4 solution; cell 0.3 mm. a) CCl_4; b) tertiary butanol C = 0.082 M; c) acetone, C = 0.102 M; d) tertiary butyl peroxide, C = 0.248 M.

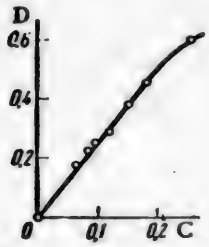

Fig. 2. Calibration curve for the determination of the absorption coefficient of tertiary butanol in CCl_4; cell 0.3 mm. D) Optical density; C) concentration in mole/liter.

Materials with the following constants were used for taking the spectra and for calibration purposes:

1. Tertiary butyl peroxide was synthesized [5] from tertiary butanol and hydrogen peroxide; b.p. 38 – 38.5 deg at 18 – 18.5 mm Hg; $n^{20}D$ 1.4012.

Published data: b.p. 38 – 38.5 deg at 18 mm Hg; $n^{20}D$ 1.4013.

2. Tertiary butanol, freshly distilled commercial grade: b.p. 82.6 deg; $n^{20}D$ 1.3876; published data: b.p. 82.9 deg; $n^{20}D$ 1.3878.

3. Commercial acetone purified by distillation, b.p. 56.4 deg; $n^{20}D$ 1.3602. Published data: b.p. 65.1; $n^{20}D$ 1.360. Purification of these materials was controlled spectroscopically.

The absorption coefficients were measured, and quantitative analysis carried out, on a modernized [3] infrared IKS-11 spectrometer, using cells specially designed for work with volatile liquids. The relation between optical density and alcohol concentration is linear up to values of the order of 0.35 mole (Fig. 2). Experimental error, which depends on the reproducibility with which the spectra can be registered, amounts to ± 3 – 1%. The values given below in the table for the concentration of synthetic mixtures also characterize the over-all accuracy of the determination.

The reaction products, in the gaseous phase, were frozen in a trap immersed in liquid nitrogen; a known volume of solvent (2 ml CCl_4) was then added and two parts of the spectrum registered at 1718 and 918 cm^{-1}. Conversion of molar concentrations to partial pressure values (in terms of mm of Hg) was carried out in the usual way.

The limiting partial pressures of the reaction products were as follows:

Tertiary butyl peroxide: from 1 to 40 mm Hg

Tertiary butanol: from 0.5 to 20 mm Hg

Acetone: from 0.5 to 25 mm Hg.

The concentration of tertiary butyl peroxide was determined iodometrically since the absorption band of CCl_4 partially overlaps the absorption band of the peroxide at 875 cm^{-1}. In any other solvent, which is transparent in this region, this particular absorption band can be used.

TABLE 1

Concentration of synthetic mixtures, in M			Concentration according to infrared analysis, in M	
CH_3COCH_3 acetone	$(CH)_3$ COH Tertiary butanol	$(CH)_3$ COOH Tertiary butyl peroxide	CH_3COCH_3 acetone	$(CH)_3$ COH Tertiary butanol
0,0114	0,085	0,248	0,0112	0,082
0,106	0,170	0,248	0,102	0,176

SUMMARY

The concentrations of acetone and tertiary butanol in the oxidation products of isobutane in the presence of HBr have been established by means of the absorption bands of these compounds at 1719 cm^{-1} and 918 cm^{-1}. The extinction coefficients of these bands to which the apparatus correction has not been applied are given. The experimental accuracy lies within the limits ±3%.

LITERATURE CITED

[1] J. H. Raley, F. F. Rust and W. F. Vaughan, J. Amer. Chem. Soc. 70, 1336 (1948).

[2] I. V. Berezin and G. B. Meluzova, J. Anal. Chem. 13, 476 (1958).*

[3] I. V. Berezin, N. F. Kazanskaia and G. B. Meluzova, J. Phys. Chem. 32, 1218 (1958).

[4] D. A. Ramsay, J. Amer. Chem. Soc. 74, 72 (1952).

[5] N. A. Milas and D. M. Surgenor, J. Amer. Chem. Soc. 68, 205 (1946).

[6] I. V. Berezin and G. B. Meluzova, J. Anal. Chem. 10, 262 (1955).*

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THE ANALYTICAL CHEMISTRY OF HAFNIUM

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Hafnium is always found together with zirconium in natural and industrial materials. Until very recently, on account of the unusual difficulties encountered in trying to separate zirconium and hafnium, it has not been possible to prepare a compound of one element free from the presence of a compound of the other [1]. When analysesare carried out, in the overwhelming majority of cases, it is the sum of zirconium and hafnium that is determined; usually it is necessary to determine one of the elements on the background of the other (in most cases it is required to determine hafnium in zirconium compounds).

A review of direct chemical methods of determining zirconium, which are also applicable to hafnium, was made recently by Portcastle [2]. In order to determine hafnium by these methods it is necessary to separate it beforehand from zirconium; for this purpose it is more convenient to use an ion exchange method considered previously [1].

Determination of hafnium in the presence of zirconium can only be carried out by certain physical methods, since completely specific and reliable reagents for the determination of hafnium or zirconium in each other's presence are not as yet available in analytical chemistry. Even some organic compounds on which some hope was placed have not yet justified themselves [3]. Many highly specific reagents for total zirconium and hafnium have been known for some time, but not for each of them taken separately.

Optical and X-ray spectrographic methods are used exclusively for the qualitative detection of hafnium in the presence of zirconium [4]. X-ray spectrographic analysis [5, 6] is particularly suitable for quantitative determination, since the X-ray spectrum of hafnium is readily distinguishable [4, 7, 8]. Details can be found in the well-known monograph of Hevesey [4], who, together with Coster, detected hafnium by means of its X-ray spectrum.

At present, chemical, physicochemical, and physical methods can be used for the quantitative determination of hafnium in the presence of zirconium.

1. Chemical and Physicochemical Methods

All known chemical methods are indirect methods. For analytical purposes it is only possible to use those few compounds of zirconium and hafnium, which, in view of their constant composition, can be obtained in a pure form without difficulty.

Analysis of Mixtures of the Tetrabromides [9] and Tetrachlorides [10], which are well-defined compounds is of equal value to the method of average atomic weights. Less suitable for this purpose is a mixture of the sulfates, since it is difficult to prepare normal sulfates which are not contaminated with excess H_2SO_4 or basic sulfates. Nevertheless, an idea of the content of hafnium in zirconium preparations can be obtained by means of this last method [11, 12].

Determination of the Ammonia Content of Precipitates of the Double Fluroammonium salts can be carried out with reasonable accuracy by distillation, after drying the mixture of hexafluorides. Knowing the ratio of the weight of ammonia in the weight of the mixture of salts, it is not difficult to calculate the content

of HfO_2 in ZrO_2 [4, 13]. The ratio of the weight of a mixture of double fluoride to the weight of a mixture of the oxides also permits the content of hafnium in zirconium to be determined [13].

The Selenite Method developed by Claasen [14], and modified later by Schumb and Pittman [15], is based on precipitation of the selenites of zirconium and hafnium from solutions of their salts by selenious acid, which has been used previously [16] for the gravimetric determination of zirconium. Initially, using selenious acid in an acid medium (0.6 N with respect to HCl or H_2SO_4 or 0.38 N with respect to HNO_3), the mixture of the basic selenites of zirconium and hafnium is quantitatively precipitated; these basic selenites, subsequently, in the presence of excess selenious acid at 80 – 100 deg slowly change (after 5 – 20 hours) into the normal selenites. The latter are dried, without decomposition, at 120 – 200 deg, and weighed (gravimetric variant).

It is possible, however, to dissolve the precipitate of selenites in dilute H_2SO_4 (containing 3% NaF) and complete the analysis by an iodometric determination of the selenious acid, based on reduction of the latter to elemental selenium (volumetric variant).

The error in both cases lies within the limits 0.9 – 1.5%. If, subsequently, zirconium and hafnium are weighed in the form of $(Zr, Hf)O_2$, it is then possible to determine the amount of hafnium indirectly in its mixtures with zirconium with an accuracy of ±0.5%. Normally, the volumetric variant is used.

The selenite method, is one of the best chemical methods, and has, accordingly, been used for the determination of atomic weights. Nevertheless, it takes a long time (25 – 30 hours), requires very pure double mixtures, and is completely unreliable for low concentrations of zirconium or hafnium in their mixtures (< 1%).

The Phosphate – Oxide Method is applicable to zirconium salts containing a few percent of hafnium [17, 18]. 50 mg of the oxides is sufficient for an analysis; they are brought into a soluble form by fusion with $KHSO_4$. Zirconium and hafnium phosphates are precipitated from the solution containing 5 – 10% H_2SO_4 by addition of an excess of a 20% solution of $(NH_4)_2HPO_4$. The precipitate, after ageing, filtering, and washing, is calcined at 1050 deg and weighed as MeP_2O_7 where Me = Zr + Hf. Afterwards, a known amount of the mixture of pyrophosphates is dissolved in 20% HF and zirconium and hafnium hydroxides precipitated by addition of a 20% solution of NaOH. After reprecipitation of the hydroxides, the precipitate is calcined and then weighed as MeO_2. From the difference in weights of the phosphates and oxides the ratio Hf/(Zr + Hf) is calculated.

A Method Involving p-Bromomandelic Acid which has been suggested previously for the determination of zirconium [19], consists of the precipitation of a mixture of the p-bromomandelates of zirconium and hafnium, and their conversion to the oxides. Precipitation is effected with 0.1 N p-bromomandelic acid taken in large excess, from a solution of zirconium and hafnium salts heated to 85 – 95 deg, and containing HCl and H_2SO_4. The precipitate is dried at 120-230° and is weighed in the form of a mixture of $Zr(C_8H_6O_3Br)_4$ and $Hf(C_8H_6O_3Br)_4$; it is then calcined at 900-1000°; the oxides of hafnium and zirconium are then weighed [20]. When samples containing more than 10% of HfO_2 are carefully analyzed by this method, an accuracy of ±0.5% (absolute error) is possible; results obtained by this method agree with those of the selenite method; at the same time analysis by the p-bromomandelic acid takes only a quarter of the time of the selenite method. Nevertheless, this method, like all other methods based on the effect of the ratio Hf/Zr on various gravimetric factors of calculation, rapidly loses in accuracy at limiting values of this ratio on account of the large effect of errors encountered during weighing, and during the various chemical operations. In particular, during the analysis of samples containing less than 10% HfO_2, high results are obtained for hafnium, and the method becomes less accurate than the selenite method.

Physicochemical methods for the determination of hafnium included spectrophotometric methods. The classical method of spectral absorption analysis, has, however, not found practical application for the determination of hafnium [21].

Spectrophotometric Methods are based on the use of certain organic derivatives of zirconium and hafnium. A large number of these reagents [3, 22] cannot be used for the determination of hafnium in the presence of zirconium. As yet it is necessary to use insignificant differences in the behavior of zirconium and hafnium towards certain organic reagents such as: rufigallic acid $C_{14}H_8O_8$ [23, 24], quinoline [25], certain hydroxyanthraquinones [26, 27], and cupferron [28].

Recently, Kuznetsov [29] has suggested a new reagent – 2, 4-disulfobenzaurine-3, 3-dicarboxylic acid – which gives yellow colored solutions, while in the presence of zirconium and hafnium the solutions acquire a rose

color. In 0.3 N HCl, both elements, at equal molar concentration, give colors of equal intensity; while in 1.2 N HCl the color given by zirconium is 2.4 times the intensity of the color given by hafnium. Light absorption is measured on a SF-4 spectrophotometer at 550 mμ. A few tenths of a milligram of each element is sufficient for determination.

The accuracy of the method is approximately 1.5 – 2% (relative) for average ratios of zirconium and hafnium, and 10 – 15% (relative) for a very small amount of one element in the other.

Spectrophotometric methods are still in the process of being developed.

2. Physical Methods

Physical methods include the following: 1) determination of density; 2) polarimetric methods; 3) radioactivation methods; 4) optical spectroscopy; 5) X-ray spectroscopy; 6) X-ray fluorescence.

Determination of the density of compounds is a fairly simple and readily carried out method for high contents of hafnium in its mixtures with zirconium. When a concentrate is rich in hafnium, even a coarse determination of the density is sufficient for analytical purposes, since hafnium compounds have a considerably greater density than zirconium: for example, the density of HfO_2 is practically twice that of ZrO_2. All the compounds of hafnium are isomorphous with the corresponding compounds of zirconium, and the molecular volumes of the mixed crystals of their compounds conform to the additivity law. The density can be measured pycnometrically [30, 31]. Usually, the density of the mixed oxides ZrO_2(d = 5.73) and HfO_2 is determined [4]. Nevertheless, the density of the oxides depends on the method of preparation, and this is reflected in the analytical accuracy; it is very difficult to determine reliably less than one percent of hafnium in a zirconium product (and vice versa). Instead of determining the density of the oxides it is possible to determine the density of $(NH_4)_2(Zr, Hf)F_6$ [7]. The high molecular weight of the hexafluorides, however, depresses the sensitivity of the method. All the same, measurement of the density of such compounds during the process of crystallizing the double fluorides may be useful as a control method during the individual stages of fractionation.

De Boer and Fast [32] have determined the density of alloys of zirconium and hafnium which were obtained during thermal dissociation of their salts. It follows, of course, that if other elements are present in addition to hafnium and zirconium, this method cannot be used. This is one of the essential drawbacks of this method, together with the fact that it is not applicable to materials containing small amounts of hafnium or zirconium.

The Polarimetric Method is based on the work of De Boer and Emmens [33], who showed that solutions containing potassium tartrate, on addition of varying amounts of zirconium and hafnium oxychlorides, exhibit a change in optical activity; they found that the effect of zirconium salts is less than that of hafnium, and that this fact can be used for the polarimetric determination of the ratio of the concentrations of zirconium and hafnium. A polarimetric method developed on the basis of these results [34] has proved to be suitable as a rapid and convenient method for controlling fractional separation of zirconium and hafnium.

Radioactivation Methods [35 – 37] are based on measurement of neutron capture cross section, or on determination of the radiation intensity of the active isotope of hafnium, obtained by neutron irradiation. According to one method [35], hafnium can be determined by a short period of irradiation (1 minute) of test material by slow neutrons. Using the hafnium isotope with τ = 20 seconds, it is possible to determine this element for contents in the test material up to 10% with an accuracy of about 5%.

According to another method [37] small amounts of hafnium and zirconium can be determined by neutron activation of hafnium, in the course of which Hf^{178} is converted into Hf^{179}, while the γ-radiation is measured by means of a scintillation counter. Using a neutron source with a flow of thermal neutrons of 5×10^6 neutrons/$/cm^2/sec$, it is possible to determine 1×10^{-4}% hafnium with an accuracy of 5%. The application of radioactivation methods is limited to special cases.

Methods of Optical Spectroscopy have been developed almost exclusively along the lines of using it for analysis of the emission spectra of hafnium, and all the successes of these methods for the determination of hafnium in zirconium (particularly of small and trace amounts of hafnium) are related to emission spectral analysis. Emission spectral analysis has the exceptional advantage over other methods that it does not require the presence of compounds of the test element (hafnium), and of the main element (zirconium), in a pure form.

The optical spectrum of hafnium has been studied in detail by Meggers [38]; it was rapidly established that

both the arc and spark spectra of hafnium [4] are suitable for the purpose of emission spectral analysis.

According to Feldman [39], determination of the ratio Hf/Zr in a sample can be carried out either with, or without, the use of preparations of pure hafnium. The test material is dissolved in 10% H_2SO_4 and the solution placed in porous graphite electrodes and then evaporated in a spark. The analytical lines used are: Hf – 2641.406 A and Zr – 2761.911 A, while the ratio Hf/Zr is calculated by means of a standard curve. Good results can be obtained for samples containing less than 1% of hafnium in zirconium. According to the method of Fassel and Anderson [40], it is possible to determine hafnium for ratios of Hf/Zr ranging from 0.001 to about 100. In this method – a spark method – tablets made from mixtures of the oxides with powdered graphite serve as conductors for the current. When internal standards are used, it is possible to determine hafnium contents within the range indicated above, with only one exposure. During accurate determinations the standard deviation amounts to 1.5 – 2%. Almost simultaneously with this method, another method was also suggested [41], which permits quantitative determination of hafnium in mixtures of HfO_2 and ZrO_2, for contents of HfO_2 ranging from 0.01 to 5%. This method which is an arc method, in which the sample is packed onto the carbon electrodes, requires not more than 10 mg of material. The best results are obtained when the following pairs of lines are used: Hf – 2631.4 A; Zr – 2647.8 A (for contents within the limits 0.01 – 1%) and Hf – 2548.2 A, Zr – 2545.6 A (for HfO_2 within the limits 0.01 – 50%. The method has a standard deviation of ±6%.

Recently, arc methods have been developed in detail for the determination of hafnium in zirconium in a narrow concentration range [42, 43]. According to one of these methods [42] it is possible to determine 0.2 – 5% of HfO_2 in ZrO_2 by exciting the spectra in a d.c. arc (220 volt, 15 amps), and using the analytical lines Hf – 2861.7 A, Zr – 2856.1 A. The mean square error for the determination of about 1.5% HfO_2 amounts to about 6%. The presence of Mg > 1%, Al > 5%, Na > 2% and Fe > 0.5% increases the experimental error because of overlapping of the lines of these elements and those of hafnium and zirconium.

According to another method [43] the concentration range within which hafnium can be determined is 0.01 – 2%. The spectrum is excited in an a.c. arc (220 volt, 23 amps). $CaCO_3$ is added to the test material in the proportion of 1:0.5 for smoother arc burning and for enhancing the sensitivity of the hafnium lines. The analytical pairs of lines used are: Hf – 2641.406 A, Zr – 2665.177 A (for concentrations of 0.01 – 0.5%), and Hf – 2641.406 A, Zr – 2665.177 A; Hf – 2351.215 A, Zr – 2351.656 A, Hf – 2641.406 A, Zr – 2643.395 A (for concentrations of 0.1 – 2%). The mean experimental error is ±7.8%.

The large number of lines in the hafnium spectrum and the low sensitivity of these lines (the most sensitive lines in the hafnium spectrum are mainly in the ultraviolet) make determination of small amounts of hafnium in minerals, ores, and waters particularly difficult. Special methods are required for the analysis of materials which are similar to each other. Thus a semiquantitative method [44] has been developed for the analysis of minerals, ores, and rocks, by means of which it is possible to determine hafnium in one operation on 10 mg of sample. The sensitivity of this method amounts to approximately 0.1% Hf. For the quantitative determination of hafnium in water, it has been suggested that the hafnium be concentrated in the form of complex compounds by extraction with chloroform and the compounds extracted, ignited on a Feisner spark. Determinations are carried out on a Zeiss spectrograph with average dispersion. 1 liter of test water is sufficient for the determination of trace amounts – from 0.5 to 1 μ g/liter. The experimental accuracy is ±10 – 20% [45].

Demands for zirconium which is almost free from hafnium, and also for pure zirconium compounds, have led to the development of new methods suitable for the determination of traces of hafnium in zirconium. Gordon and Jacobs have used an arc method for this purpose [46]. In order to excite the spectrum, powdered metal or oxide is charged into the crater of a graphite electrode, and evaporated in a d.c. or a.c. arc. Using a Hilger spectrograph and using standards, the authors have shown that it is possible to determine 1×10^{-3}% of hafnium; the accuracy, however, is only ±30%. The best methods developed recently are those of Martimore and Noble, [47] and those of Russian workers [48, 49].

The method of Mortimore and Noble which is a further development of that described earlier by Spitzer and Smith [50], is based on excitation of samples of ZrO_2 in a d.c. arc at a current of 30 amps. and 230 volts. The samples are prepared from a mixture of 25 mg of ZrO_2 and 20 mg of a buffer mixture composed of a BaF_2 and graphite powder in the ratio 1:1. The authors used a spectrograph with a dispersion of 1.6 A/mm in the third order spectrum. The method permits quantitative determination of 0.003 to 0.4% of hafnium. For concentrations of 0.003 – 0.1%, the intensity of lines of the third order are compared: Hf – 2720.2 A and Zr – 2820.6 A, while for concentrations of 0.03 – 0.4% Hf, the same hafnium line is used with the zirconium line 2823.0 A – third

order. The accuracy of the method, depending on the hafnium concentration (0.006 – 0.4%), varies within the limits 13 – 4%. In order to attain the good accuracy, and very high sensitivity which is characteristic of this method, it is necessary to use a spectrograph which not only has a high resolving power, but is also provided with special filters.

Russian workers [48, 49] have solved the problem of determining hafnium in zirconium on a spectrograph with average dispersion (ISP-22). In one of the methods [48] for evaporation from the crater of the carbon electrodes, use is made of a mixture (Zr, Hf)O_2, graphite, and sodium pyrophosphate in the proportions 4:4:1. Spectrum excitation is effected with a d.c. arc (9 amps, 240 volts); analysis is carried out on the basis of the following pairs of lines: Hf – 2393.83 A; Zr – 2392.68 A and Hf – 2417.69 A; Zr – 2416.88 A. Standard samples are used for constructing a calibration curve. The method covers the concentration range 0.01 – 0.02 to 15% of hafnium in zirconium. The mean experimental error is ±5 – 8%.

In another method [49] suggested for the determination of hafnium in minerals, ores, and processed products, both arc and spark variants have been developed. In the arc variant 5 mg of (Zr, Hf)O_2 or the natural products is placed in the crater of the positive electrode, and the spectrum excited with a d.c. arc (9 amps, 240 volts). The analytical lines used are: Hf – 2738.7 A; Zr – 2754.2 A or Hf – 2622.7 A, Zr – 2630.9 A. The concentration range covered by the method is 0.1 – 55% HfO_2 in ZrO_2; the error for a single determination is ±8 – 10%. A Feisner arc generator is used in the spark variant for exciting the spectrum. Tablets made from a compressed mixture composed of 75% silver and 25% of the oxides of hafnium and zirconium are subjected to excitation. The analytical lines used are: Hf – 2641.4 A, Zr – 2643.4 A or Hf – 2551.4 A; Zr – 2550.7 A. The concentration range covered is 0.5 – 82% of HfO_2 in ZrO_2; the experimental accuracy is ±5%.

The X-Ray Spectrographic Method is, probably, the most reliable, in those cases where one has to deal with determination of elements whose electronic orbits are similar in structure. The X-ray spectrum of the short-wave K and L series of atoms is characterized by a small number of lines which maintain their relative intensity and their mutual arrangement for most elements. The advantages of X-ray spectrographic analysis over other methods for the determination of hafnium in minerals, particularly in silicates [4], ores and enrichment products [51] are well-known; it has even been suggested [52] that for this purpose, X-ray spectrographic analysis is the only one applicable.

X-ray spectrographic determination of hafnium, first carried out by Coster [5], is based on mixing the test material containing hafnium with a known amount of a compound of the reference element, having adjacent atomic numbers – Lu or Ta, and the ratio of the atomic contents of a mixture of these elements established, for which the intensity of the chosen analytical lines is the same (method of "blackening equalization").

In the first investigations of Coster [5], and Hevesy and co-workers[4, 53, 54], the reference element used was tantalum; the last two research workers were compelled to abandon this element because of the high results they obtained. This is explained by the fact that in certain orders of reflection, the most intense lines of zirconium and the important analytical lines of hafnium almost completely overlap each other (L-series), while some of the hafnium lines coincide with some tantalum lines [55]. When lutecium was used [54-56], the lines L and L_{β_2} (λ = 1367.26 A) were used for reference, while the analysis was based on the line $HfL_{\beta 1}$ (λ = 1371.25 A), the intensity of which is approximately 50% of the intensity of HfL_{α_1}.

Subsequently, the research workers [52] returned again to tantalum as a reference element, this time introducing it into the test material as Ta_2P_5. For Hf contents less than 1% the intensity of the line HfL_{β} and the coinciding lines of TaL_{β_1} and HfL_{β_2}. For Hf contents greater than 1%, the shortest line of the L-spectrum was used (γ_1). By comparing the relative intensity of the lines HfL_{γ} (λ = 1176.56 H units) and TaL_{γ} (λ = 1135.64 H units), and, knowing the amount of tantalum added, it is possible to determine the amount of hafnium.

At present the accuracy of the X-ray spectrographic method for the determination of hafnium and zirconium has been increased significantly, while the duration of analysis has been cut down. A method developed recently [57] covers the concentration range 0.5 to 99.5% hafnium, and gives a mean deviation of 3.3% for samples containing 1% Hf, and 0.5% for samples with 40% Hf. Good results have been obtained during the determination of small amounts of hafnium in zirconium minerals, on the basis of the most intense lines in the X-ray spectrum of this element [58]. For series determinations of hafnium in raw material and processed material, interpolation on the basis of standards is used; for preparing the latter, zircon or synthetic mixtures, carefully analyzed beforehand for their hafnium content, can be used. Quantitative determination of hafnium by the given

method is possible starting with 0.2 – 0.3% of Hf. The reproducibility and mean experimental error are approximately 6%.

In the Method of X-Ray Fluorescence the fluorescence spectrum is not excited by a cathode beam inside the X-ray tube, but by the primary X-rays [59 – 64]. Good results are possible with mixtures containing more than 20% of hafnium [60], or during determination of very low concentrations [65] and even of trace amounts [63, 64]; however, in the latter instance, the error may be as high as 13% [63]. Analysis of minerals and concentrates for contents of hafnium ranging from 0.1 to 5% can be carried out with an accuracy of ±5 – 10% [61 – 67].

At the present level of development, the X-ray fluorescence method is most suitable for semiquantitative, and mainly for qualitative analysis, since, in the latter instance, it does not require any treatment of the material. In the remaining instances, it should be borne in mind that the fluorescence spectra are very weak, and this means that it is necessary to use very powerful tubes, or increase the sensitivity of the recording of the spectra.

All the same, the X-ray fluorescence method is being improved rapidly, and is opening up new possibilities for the analysis of complex materials, in particular, for the determination of hafnium in zirconium. Recently, Narbutt and Bespalova [67] managed to achieve good resolution of the analytical lines of hafnium and zirconium by using a universal focussing X-ray spectrometer with a curved crystal (the transmission method). The comparatively high dispersion of the apparatus (10 H units/mm when operating at the first order of reflection, and 5 H units/mm at the second order) excluded any interference during the analysis arising from overlapping of spectral lines.

LITERATURE CITED

[1] L. N. Komissarova and V. E. Pliushchev, Prog. Chem. 25, 1197 (1956).

[2] T. O. Portcastle, Chem. Age 68, 389, 533, 673, 741 (1953).

[3] V. I. Kuznetsov, Trans. All-Union Conference on Anal. Chem. Izd AN SSSR, 1, Moscow – Leningrad, 81 (1938).

[4] G. Hevesey, "X-Ray Chemical Analysis and its Applications," [Translated from English] GNTI, Moscow – Leningrad (1940).

[5] D. Z. Coster, Electrochem. 29, 344 (1923); Chem. Weekl. 20, 122 (1923).

[6] K. Kimura, Z. phys. Chem. 128, 394 (1927).

[7] G. Hevesy, Das Element Hafnium, Berlin (1927).

[8] H. Rose, Das Hafnium, Braunschweig, (1926).

[9] O. Hönigschmid, E. Zintl and F. Ganzalez, Z. anorgan. und allgem. Chem 139, 293 (1924).

[10] F. P. Venable and J. M. Bell, J. Amer. Chem. Soc. 46, 1833 (1924).

[11] G. Hevesy, Ber. 56, 1503 (1923).

[12] P. Urbain and G. Urbain, Compt. rend. 178, 265 (1924).

[13] G. Hevesy, Chem. Rev. 2, 2 (1925).

[14] A. Claasen, Z. analyt. Chem. 117, 252 (1939).

[15] W. C. Schumb and F. K. Pittman, Ind. Eng. Chem., Anal. Ed. 14, 512 (1942).

[16] S. G. Simpson and W. C. Schumb, J. Amer. Chem. Soc. 53, 921 (1931).

[17] Shizuo Fujiwara, Bunseki to Shiyaku (Chem. Analysis and Reagent) 2, 241 (1948); Chem. Abstrs. 46, 10047 (1952).

[18] Shizuo Fujiwara, J. Chem. Soc. Japan, Pure Chem. Sect., 70, 129 (1946); Chem. Abstrs., 45, 4171 (1951).

[19] R. E. Oesper and J. J. Klingenberg, Analyt. Chem. 21, 1509 (1949).

[20] R. B. Hahn, Analyt. Chem. 23, 1259 (1951).

[21] R. Glocker and W. Frohnmayer, Ann. Phys. [5], 76; 369 (1925).

[22] A. Okac, Chem. Obzor. 14, 203 (1939).

[23] I. H. De Boer, Rec. Trav. chim. 44, 171 (1925).

[24] A. Okac, Chem. Listy 39, 61 (1945).

[25] C. J. van Nieuwenburg and J. W. van Ligten, Analyt. chim. acta 7, 390 (1952).

[26] H. A. Liebhafsky and E. H. Winslow, J. Amer. Chem. Soc. 60, 1776 (1938).

[27] H. A. Liebhafsky and E. H. Winslow, J. Amer. Chem. Soc. 69, 1130 (1947).

[28] S. Fujiwara, Ref. Chem. J., No. 2, 250 (1956).

[29] V. I. Kuznetsov and A. A. Nemodruk, Reports read at the Conference on Spectrophotometric and Colorimetric Methods of Analysis; Izd AN SSSR, Moscow, 46 (1955).•

[30] G. Hevesy and V. Berglund, J. Chem. Soc. 125, 2372 (1924).

[31] E. M. Larsen, W. C. Fernelius and L. L. Quil, Ind. Eng. Chem., Anal. Ed. 15, 512 (1943).

[32] I. H. De Boer and J. D. Fast, Z. anorgan. und allgem. Chem. 187, 193 (1930).

[33] I. H. De Boer and H. Emmens, Rec. trav. chim. 49, 955 (1930).

[34] G. Wernimont and T. de Vries, J. Amer. Chem. Soc. 57, 2386 (1935).

[35] A. H. Aten and Tijdschr Niderland, Natuurkunde 10, 257 (1943); Chem. Abstrs. 40, 4950 (1946).

[36] A. Smales, Atomics 4, 55 (1953).

[37] Th. Stribel, Z. angew. Math. und Phys. 9, 293 (1957).

[38] W. Meggers, Bureau Standards J. Research 1, 151 (1928).

[39] C. Feldman, Analyt. Chem. 21, 1211 (1949).

[40] V. A. Fassel and Ch. H. B. Anderson, J. opt. Soc. Amer. 40, 742 (1950).

[41] G. W. Kingsbury and R. J. Temple, Appl. Chem. 1, 460, (1951).

[42] R. K. Dhumwad and M. D. Karkhanavala, Analyt. chimica acta 15, 87 (1956).

[43] Nakano, Morita, Ref. Chem. J. No. 2, 110 (1958), Repts. govt. Ind. Res. Inst. Nagoya (1957); 6, 163 (1957).

[44] C. L. Waring and C. S. Annell, Analyt. Chem. 25, 1174 (1953).

[45] F. A. Pohe, Z. analyt. Chem. 139, 241 (1953).

[46] N. E. Gordon and R. M. Jacobs, Analyt. Chem. 25, 1605 (1953).

[47] D. M. Mortimore and L. A. Noble, Analyt. Chem. 25, 296 (1953).

[48] G. Kriuger, R. R. Shvangiradze and T. A. Mozgovaia, J. Anal. Chem. 10, 20 (1955).••

[49] E. V. Gusiatskaia and A. K. Rusanov, J. Anal. Chem. 10, 75 (1955).••

[50] E. J. Spitzer and D. D. Smith, Applied Spectroscopy 6, 9 (1952).

[51] I. B. Borovskii, Trans. All-Union Conference on Anal. Chem. 1, Izd AN SSSR, Moscow – Leningrad, p. 135 (1939).

[52] I. B. Borovskii and M. A. Blokhin, Bull. Acad. Sci. USSR. Geol. Series, No. 1, 185 (1937).

[53] G. Hevesy and J. Böhm, anorgan. und allgem. Chem. 164, 69 (1924).

[54] G. Hevesy and V. T. Jantzen, Naturwiss 12, 730 (1924).

• In Russian.

•• Original Russian pagination. See C.B. Translation.

[55] E. E. Vainshtein and M. M. Kakhana, "Reference Tables on X-Ray Spectroscopy," [In Russian] Izd AN SSSR, Moscow, (1953).

[56] D. Coster and Y. Nishina, Chem. News 130, 149 (1925).

[57] D. M. Mortimore and P. A. Roman, J. Opt. Soc. America 42, 673 (1952).

[58] E. E. Vainshtein, N. D. Shevaleevskii and I. F. Shtauberg, J. Anal. Chem. 10, 14 (1955).*

[59] H. Friedman and L. Birks, Rev. Sci Instruments 19, 323 (1948).

[60] P. D. Zemany, E. H. Winslow, G. S. Poellmitz and H. A. Liebhafsky, Analyt. Chem. 21, 493 (1949).

[61] L. S. Birks and E. J. Brooks, Analyt. Chem. 22, 1017 (1950).

[62] L. S. Birks, E. J. Brooks and H. Friedman, Analyt. Chem. 25, 692 (1953).

[63] L. S. Birks and E. J. Brooks, Analyt. Chem. 27, 437 (1955).

[64] K. I. Narbutt, Factory Labs. 24, 604 (1958).

[65] J. Despujols and D. Lumbroso, J. chim.-phys. et phys.-chim. biol. 53, 108 (1956).

[66] W. J. Campbell and H. F. Carl, Analyt. Chem. 26, 800 (1954).

[67] K. I. Narbutt and I. D. Bespalova, Factory Labs. 24, 617 (1958).

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BRIEF COMMUNICATIONS

A RAPID METHOD FOR THE ANALYSIS OF CLINKER AND CEMENT

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During the rapid analysis of clinker and Portland cement, the test material is dissolved in hydrochloric acid, while the silicon is removed and determined by the gelatine method. Iron, aluminum, and titanium are precipitated from the filtrate by means of ammonia; this precipitate is dissolved in hydrochloric acid and aluminum determined in the solution by the fluoride method. Iron and titanium are determined on a separate aliquot by a complexonometric method; calcium and magnesium are also determined on the filtrate freed from R_2O_3 by a complexonometric method.

The total sulfate content is determined on a separate aliquot by calcining at 1200 – 1300 deg and titrating the SO_2 liberated with iodine. Calcium sulfate (gypsum) is determined by means of an ion exchange resin. The alkali metals are determined by flame photometry.

TABLE 1

Determination of Silica

Expt. No.	Found, in %		Difference, in %
	HCl	gelatine	
1	20.68	20.60	−0.06
2	21.19	21.10	−0.09
3	23.25	23.40	+0.15
4	23.51	23.55	+0.04
5	30.40	30.29	−0.11
6	30.85	30.98	+0.13

TABLE 2

Determination of Iron

Expt. No.	Fe_2O_3 found, in %		Difference, in %
	$KMnO_4$	Complexometric	
1	2.94	2.89	−0.05
2	3.03	2.87	−0.16
3	4.83	4.72	−0.11
4	6.60	6.45	−0.15
5	2.70	2.70	−0.00
6	3.63	3.54	−0.09

Free lime (CaO) is determined complexonometrically.

Experimental results are given in Tables 1 – 6.

Method. About 0.5 g of sample is placed in a 250 ml beaker (low type), moistened with a few drops of water, and 20 – 30 ml of hydrochloric acid added (sp.gr. 1.19), the whole is then heated to the boil and boiled for 5 – 6 minutes; after cooling to 70 ± 5 deg, 3 – 4 ml of 2% gelatine solution heated to 70 deg is then added to the solution with continuous stirring. The solution is kept on a water bath (70 deg) for 10 minutes and is then filtered through a "white band" filter paper. The precipitate is washed, dried, and calcined at 1000 deg, and finally weighed. For the most accurate analysis the precipitate is treated with hydrofluoric acid in the presence of sulfuric acid and the residue calcined. The difference in weight gives the amount of pure silicic acid. The residue is fused with sodium carbonate and the melt obtained dissolved in hydrochloric acid; the solution obtained is added to the main filtrate.

The filtrate obtained after removal of the silicic acid is heated to 60 – 70 deg and ammonia added until a neutral reaction is given (litmus). The precipitate is washed and then dissolved in hydrochloric acid (1:2). The aluminum content of the solution thus obtained is determined. The solution is neutralized with NaOH (20%) – free from sodium carbonate – to a weak reddening of Congo paper. 20 – 30 ml of a 20% solution of sodium potassium tartrate is added followed by 5 – 6 drops of phenophthalein, and the solution neutralized with sodium hydroxide to the appearance of a stable red color; the red color is destroyed by addition of 1 drop of 0.1 N hydrochloric acid. To this neutral solution is added 1 ml of a 30% solution of potassium fluoride and the potassium hydroxide liberated titrated with 0.1 N hydrochloric acid until the solution is colorless. Another 1 ml of potassium fluoride solution is added and titration again carried out with hydrochloric acid. This process is continued until addition of a further new portion of potassium fluoride solution does not lead to any change in color of the solution.

Iron and titanium are determined separately. For this purpose 0.5 – 1 g of test material is dissolved in a beaker in 30 – 40 ml of hydrochloric acid on addition of 1 – 2 ml of dilute nitric acid; the solution obtained is transferred to a 250 ml standard flask and is made up to the mark with water.

In order to determine iron, 100 ml of this solution is transferred to a 250 ml conical flask, ammonia is then added until a precipitate appears; the latter is dissolved by addition of one drop of hydrochloric acid. The pH is carefully adjusted to a pH of 1 – 2, and the solution heated to 50 deg; 0.5 – 1 ml of a 10% alcoholic solution of salicylic acid is added and the solution titrated with 0.05 M Complexon III solution, with constant agitation, until the blue-violet color of the solution changes to a pure yellow with a green tinge. A standard solution is used for reference.

TABLE 3

Determination of Calcium

Expt. No.	CaO found, in %		Difference, in %
	Gravimetrically	Complexonometrically	
1	65.14	65.10	−0.04
2	60.20	60.25	+0.05
3	62.70	62.60	−0.10
4	58.70	58.55	−0.15
5	57.19	57.13	−0.06
6	56.41	56.35	−0.06

TABLE 4

Determination of Magnesium

Expt. No.	MgO found, in %		Difference, in %
	Gravimetrically	Complexonometrically	
1	0.46	0.50	+0.04
2	1.10	0.95	−0.15
3	1.13	1.20	+0.07
4	1.76	1.65	−0.11
5	3.79	3.60	−0.19
6	1.30	1.40	+0.10

1 ml of 0.05 M Complexon III solution corresponds to 0.003992 g of ferric oxide.

Titanium is determined by transferring 100 ml of the solution to another conical flask, and ammonia is then added until a precipitate appears, this precipitate is dissolved by addition of one drop of hydrochloric acid, and the pH adjusted to 1 – 2; the solution obtained is heated to 50 deg and 0.5 – 1 ml of a 10% alcoholic solution of salicylic acid added. The solution thereupon acquires a blue-violet color. A drop of hydrogen peroxide is added and the solution turns a red-brown color. The solution is finally titrated with 0.05 M Complexon III solution until a pure yellow color with a green tinge is obtained.

The difference in the volume of Complexon III solution used in the two titrations corresponds to the amount of titanium. 1 ml of 0.05 M Complexon III solution corresponds to 0.003995 g of TiO_2.

Calcium and magnesium are determined in the filtrate which is diluted to the mark in a 250 ml standard flask.

In order to determine calcium, 50 ml of the solution is transferred to a 250 ml beaker and sodium hydroxide (20%) added until the pH is 12 (indicator paper is used for controlling the pH); murexide (mixed with sodium chloride) is then added, and the solution titrated, with continuous agitation, with 0.05 M Complexon III solution, until the cherry color changes to a blue-violet.

1 ml of 0.05 M Complexon III solution corresponds to 0.00280 g CaO.

For determination of magnesium, 10 ml of a buffer solution (ammonia + ammonium chloride) is added to 50 ml of the solution contained in a 250 ml beaker; Eriochrome Black T (mixed with sodium chloride, or in solution) is added and the solution titrated, with continuous agitation, with 0.05 M Complexon III solution until the color of the solution changes from a cherry-red to a pure blue. The difference between the second and first titers corresponds to the amount of magnesium. 1 ml of Complexon III solution corresponds to 0.0020 g MgO.

TABLE 5

Determination of Sulfates

Taken, in g	Found, in g	Difference, in g
0.0110	0.0110	−0.000
0.0170	0.0171	−0.0001
0.02500	0.0242	−0.0008
0.0322	0.0310	−0.0012
0.0339	0.0329	−0.0010
0.0533	0.0520	−0.0013

TABLE 6

Determination of Gypsum

Taken, in g	Found, in g	Difference, in g
0.0190	0.0190	−0.000
0.0200	0.0189	−0.0011
0.0218	0.0216	−0.0002
0.0255	0.0250	−0.0005
0.0363	0.0355	−0.0008
0.0138	0.0132	−0.0006

The alkali metals are determined flame-photometrically on a separate aliquot, after treatment with hydrofluoric acid in the presence of sulfuric acid.

When samples of cement or clinker are calcined at 1200 − 1300 deg in a Mars oven (the same apparatus as that used for the determination of sulfur in steel) sulfur dioxide is liberated quantitatively and is titrated with 0.01 N iodine solution; the latter is standardized against a sample with a known sulfate content. In this way the sulfate content of cement can be determined in a few minutes.

The calcium sulfate (gypsum) content is determined on a separate aliquot. 0.5 − 1 g of the cement is treated twice with 50 ml of water and the washings filtered off. The filtrate is passed through a column packed with Wofatite and the column washed with water until the eluates no longer give an acid reaction (methyl orange). The solution obtained is titrated with 0.1 N sodium hydroxide. 1 ml of 0.1 N sodium hydroxide corresponds to 0.0068 g of $CaSO_4$ or 0.0040 g SO_3.

The difference between the two determinations corresponds to the amount of sulfate in the clinker.

To 1 g of sample contained in a conical flask is added 6 ml of ethyl acetate, 40 ml of isobutanol, and 10 − 15 ml of diethylether. This mixture is refluxed for 1 hour, after which it is filtered through a glass filter; the residue is finally washed 3 − 4 times with a mixture of ethyl acetate and isobutanol in the same proportion. The filtrate is transferred to a separating funnel and 20 ml of a 1% solution of hydrochloric acid added; the whole is then vigorously shaken. After a few minutes the lower layer is transferred to a beaker for titration. The extraction is repeated twice again. NaOH is added to the combined solution until the pH is 12, murexide is added and the solution titrated with 0.025 M Complexon III solution until the wine-red color changes to blue-violet.

1 ml of 0.025 M Complexon III solution corresponds to 0.001402 g free CaO.

SUMMARY

A rapid method is described for the determination of Si, Fe, Al, Ti, Ca, Mg, SO_4, $CaSO_4$, and free CaO in clinker and Portland cement.

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DETERMINATION OF PEROXIDE COMPOUNDS IN PYROLYSIS TAR

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There are a number of methods for determination of peroxides [1 – 6]. They are all based on reduction of the peroxides, and differ from each other in the nature of the reducing agents and solvents used. The presence of unsaturated compounds leads to considerable difficulties. During the determination of peroxides in the presence of unsaturated hydrocarbons by Wilson and Jull's method [3] using $FeSO_4$, low results are obtained, while at low concentrations the method is not applicable. Paniushkina and Gindina [7]* were unable to determine the content of peroxides in tar by a modified method, as a result of the formation of clots of tar (unsaturated polymers) and formation of a deposit of potassium sulfate.

The arsenite method [8] makes it possible to determine peroxides in the presence of unsaturated hydrocarbons; it is based on reduction of peroxides by arsenite with subsequent iodometric determination of excess arsenite.

Experimental Procedure. Into a long funnel are introduced 75 ml of water, 2.0 ml of 0.1 N sodium hydroxide, 2 drops of phenolphthalein, and, depending on the expected peroxide content, 10.0 – 0.5 ml of pyrolysis-tar distillate boiling up to 200 deg, and 50 ml of 0.05 N sodium arsenite. The volume of the upper layer should amount to 50 – 100 ml. The mixture is transferred to a flask which is connected via a ground-glass joint to a spherical condenser, and the funnel rinsed with 25 ml of 95% ethanol. CO_2 is passed through the flask, and, with the CO_2 still passing through, and the mixture giving an alkaline reaction to litmus, the whole is heated for one hour under efficient reflux. The mixture is then acidified with 1.0 N sulfuric acid, heating is discontinued and the mixture allowed to cool in a stream of CO_2. The mixture is transferred to a separating funnel and the lower layer extracted three times with 25 ml lots of chloroform. The chloroform is removed and the solution cooled with ice. 1 g of Na_2CO_3 is then added and the solution titrated with iodine using starch as indicator. A blank is carried out at the same time.

For small amounts of peroxides, in order to increase the sensitivity of the method, an organic solvent is used. The reddish-violet color of a solution of iodine in carbon tetrachloride or chloroform is detectable at iodine concentrations which cannot be detected by the iodine-starch reaction.

TABLE

Taken	Milliequivalents of active oxygen per liter of sample		
	Found		
	Iodometrically	By the arsenite method	Method [3]
0.5	0.46	0.51	0.17
1.9	1.62	1.88	0.06
3.65	3.02	3.72	2.01
3.54	3.10	3.60	1.76
1.625	1.20	1.58	0.98

The peroxide number (the milliequivalents of active oxygen per liter of sample) is calculated by means of the formula:

$$\frac{1000 \cdot N \cdot (a - b)}{c},$$

where a is the number of mls of iodine used for the blank; b is the number of mls of iodine used for titrating the sample; c the volume of sample taken for analysis; N the normality of the iodine solution. Boiling for one hour is sufficient for ensuring that the reaction goes to completion.

* As in original – Publisher's note.

As the results given in the Table show, peroxides can be determined in the presence of unsaturated hydrocarbons with a high degree of accuracy when the arsenite method is used.

Since excess arsenite is determined only after organic impurities have been extracted from the mixture, the weight of sample that can be taken for analysis can be made quite large, so that when the arsenite method is used, it is possible to determine traces of peroxide which could not determined by the iodometric method.

SUMMARY

An arsenite method for determination of peroxides in the presence of unsaturated hydrocarbons is described. The method is based on reduction of the peroxides with arsenite followed by iodometric titration of excess arsenite.

LITERATURE CITED

[1] N. N. Dastur and C. H. Lea, Analyst 66, 90 (1941).

[2] V. D. Kokathur and M. J. Jelling, J. Amer. Chem. Soc. 63, 1432 (1941).

[3] C. D. Wilson and J. A. Jull, Ind. Eng. Chem. 23, 1254 (1931).

[4] C. A. Lea, J. Soc. Chem. Ind. 65, 286 (1946).

[5] C. D. Wagner and R. H. Smith, Anal. Chem. 19, 976 (1947).

[6] D. Mitchell and D. Smith, "Aquametry," [Translated from English], IL, Moscow, p. 361 (1952).

[7] M. A. Il'inskii, Bull. Acad. Sci. SSSR, Chem. Series, No. 4, 841 (1938).

[8] C. D. Walker and H. S. Conway, Anal. Chem. 25, N 6, 923 (1953).

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ERRATA

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Page	Line	Reads	Should read
437	Formula 5	$\chi^2(\int - 1) \approx$	$\chi^2/(\int - 1) \approx$
456	2nd from top	$\cdot 2H_2O$ (Mn/ OH $)_4$	$\cdot 2H_2O$ [Mn(OH)$_4$]
457	2nd from top	$MnNH_4PO_6$	$MnNH_4PO_4$
457	8th from top in 5th column of table	±0.9	+0.9
458	20th from bottom	$2IO^- + 4H_2O - 8e = 2IO + 8H^+$	$2IO^- + 4H_2O - 8e = 2IO_3^- + 8H^+$
458	17th from bottom	$2IO^- + 2IO^- + 2Cl^- + 4H^+$	$2IO^- + 2Cl^- + 4H^+$
459	6th from top	or $Hg + H^+$	or $HgO + H^+$
459	[4] lit. cit.	(1950)	(1930)
460	[13] lit. cit.	Vol. 11	Vol. 2
477	Heading	Microcrystalline	Microcrystalloscopic
495	in the formula	2-hydroxy-3-chloro-5-nitrobenzene-(1-azo-2)-1'-hydroxy-8'-alinonaphthalene-3',6'-disulfonic acid	2-hydroxy-3-chloro-5-nitrobenzene-(1-azo-2)-1'-hydroxy-8'-aminonaphthalene-3',6'-disulfonic acid
549	8th from bottom	2.60 g − 0.25 g = 2.35 g	2.60 g − 0.26 g = 2.34 g
549	4th from bottom	1.65	1.55

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